KFe$_2$As$_2$: coexistence of superconductivity and local moment derived spin-glass phases

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High-quality KFe$_2$As$_2$ single crystals have been studied by transport, magnetization and low-$T$ specific heat measurements. Their analysis shows that superconductivity occurs (in some cases coexists) in the vicinity of disordered magnetic phases (Griffiths and spin glass type) depending of the amount of local magnetic moments (probably excess Fe derived) and sample inhomogeneity. The achieved phenomenological description including also data from the literature provides a consistent explanation of the observed non-Fermi-liquid behavior and of the *nominally* large experimental Sommerfeld coefficient $\gamma_n \approx 94\,\text{mJ/molK}^2$. We suggest that the intrinsic value (directly related to the itinerant quasi-particles) $\gamma_{cl} \approx 60(10)\,\text{mJ/molK}^2$ is significantly reduced compared with $\gamma_n$. Then an enhanced $\Delta C_{el}/\gamma_{cl} T_c \sim 0.8$ and a weak total electron-boson coupling constant $\lambda \lesssim 1$ follow.

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The nature of the superconductivity in KFe$_2$As$_2$ (K122) is under debate \cite{1,2,11}. This is due to its distinctive characteristics with respect to other Fe-pnictides: its heavily hole doping is responsible for the lacking nesting of the Fermi surface in contrast to less hole-doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ \cite{3}. For instance, a neutron scattering study of K122 revealed well-defined low-energy incommensurate spin fluctuations at $[\pi(1 \pm \delta), 0]$ with $\delta = 0.16$ \cite{2}. Also, NMR studies suggest that a type of AFM spin fluctuations *different from* that of the undoped (Ba, Ca, Sr)122 parent compounds develops in K122 \cite{4}. A strong or sizable effective mass enhancement of the quasi-particles has been observed in de Haas-van Alphen \cite{5,6} and cyclotron resonance \cite{7} measurements, respectively. Additionally, ARPES-data also point to strong band renormalization which suggest an effective mass enhancement by a factor of 2-4 \cite{3}. The Sommerfeld coefficient $\gamma_n \sim 70-100\,\text{mJ/molK}^2$ from the linear specific heat (SH) \cite{11,13} is strongly enhanced compared with the reported (from band structure density of states (DOS) derived) "bare" values $\gamma_{cl} \sim 10.1$ \cite{12,14} or 13 (mJ/molK$^2$) \cite{8} adopted from DFT-calculations. To the best of our knowledge, only for one, very clean, sample with RRR$_5 = \rho(300\,\text{K})/\rho(5\,\text{K}) \approx 480$, a convincing $\rho \propto T^2$ was observed at low $T = 5 - 10\,\text{K}$ evidencing standard Fermi-liquid behavior (FLB) \cite{8}. But for less perfect samples with RRR$_5 \approx 86$ the resistivity follows a different, *subsquered* power-law: $\rho \propto T^{1.5}$ above $T_c$ \cite{12}, whose authors considered this $T^{1.5}$-law as a signature of spin fluctuations in a clean 3D-AFM. From the analysis of SH-data it was concluded that non-Fermi-liquid behavior (NFLB) can be related to magnetic impurities \cite{12}. At low $T \ll T_c$, a further not yet fully understood magnetic anomaly has been observed. In this situation, the elucidation of the pairing symmetry is a delicate problem and a clear understanding of various coexisting or competing forms of magnetism should be addressed first.

Similarly as for La-1111 \cite{12}, Co and K doped 122 \cite{11,12}, we suppose that point defects might induce local magnetic moments (LM) also in K122. Recently, we have shown that LM in pnictides can be formed e.g. around As vacancies \cite{12}. At variance with La-1111 superconductors where such LM only enhance the spin susceptibility \cite{12}, in K122 even a very small amount of them leads to the formation of disordered magnetic phases such as spin glass (SG) and Griffiths (G) phases. By analyzing carefully the low-$T$ behavior of $\rho(T)$, the magnetic susceptibility $\chi(T)$, and SH data for K122 single crystals with different amount of disorder, we will show that most of their anomalous properties listed above are related to the vicinity and even to the coexistence of superconductivity with these magnetic phases. This naturally explains the NFLB of $\rho(T)$ and the unexpectedly high value of $\gamma_n$ obtained from low-$T$ SH data.

K122 single crystals have been grown using a self-flux method (FeAs-flux (S1) and KAs-flux (S2)), for description see \cite{13,20}. Low-$T$ SH, ac susceptibility and four-probe resistivity were determined using a PPMS from Quantum Design. The dc magnetic susceptibility has been measured in a SQUID Quantum Design magnetometer. Fig. (1a) presents the $T$-dependence of the in-plane electrical resistivity $\rho$ for both K122 single crystals S1 and S2. Upon cooling the $\rho$ decreases monotonically showing a metallic behavior at all $T$ with a RRR$_5 \approx 380$ for crystal S1 and 400 for S2. Below 10K the resistivity of both crystals shows NFLB: $\rho(T) = \rho_0 + AT^n$ with $1.5 < n < 2$ (Fig. (1b)). Noteworthy, our $\alpha$ differs from 1.5 reported for less perfect crystals with RRR$_5 \approx 86$ \cite{12}, only, and from 2 for the cleanest available case RRR$_5 \approx 480$ \cite{8} where FLB has been reported. In this context we stress that the reported $T^2$-law for samples with RRR$_5 \sim 80$ and $T_c = 2.8\,\text{K}$, only, in Ref. \cite{21} might be related to a *too large* fit region up to 45 K used there. In fact, we observed that too broad $T$-ranges can *mask* deviations from the FLB \cite{22}. Our samples have rather high transition temperatures: $T_{c}^{\rho=0.05\%}=3.85(10)$ K for sample S1 and $3.95(10)$ K for sample S2 (Fig. (1a)) comparable with the high $T_c$-values of other single crystals with large RRR values \cite{8,12,13}.

Fig. (2) (a) depicts the $T$-dependence of the susceptibil-
ity determined from the dc magnetization of our samples measured under both zero-field-cooled (ZFC) and field-cooled (FC) conditions with the field $B = 20$ Oe applied $\parallel ab$. Bulk superconductivity of our samples is confirmed by the sharp diamagnetic signal of the ZFC data at low $T$. Sample S2 does not show any difference between ZFC and FC curves above $T_c$. But for sample S1, a clear splitting is observed below 100 K (see the inset of Fig. 1(a)). The kink in the ZFC data is attributed to the freezing of two K122 single crystals measured in zero-field up to $\rho$ by the sharp diamagnetic signal of the ZFC data at low $T$. Sample S2 does not show any difference between ZFC and FC curves above $T_c$. But for sample S1, a clear splitting is observed below 100 K (see the inset of Fig. 2(a)). In addition to the ZFC splitting an frequency-dependence of the ac susceptibility (see inset Fig. 2(b)) was observed for crystal S1. Such a behavior is generic for a spin-glass phase $\mathbf{23}$, $\mathbf{24}$. In view of the INS data $\mathbf{2}$ one might assume that few magnetic impurities might convert locally the incommensurate SDW from an excited state in the clean limit to a pinned SDW-type phase, and finally to a glassy state below $T_f \approx 60$ K. Further studies are desirable to improve quantitatively such a scenario obtained originally under simplifying assumptions. In contrast, the analysis of the $T$-dependence for the susceptibility of sample S2 measured at different fields doesn’t show any magnetic transition. On the other hand, at $T > 30$ K the susceptibilities of our two crystals exhibit similar $T$-dependencies as shown in Fig. 2(b) by choosing a proper $T$-range. We suppose that the magnetic defects of crystal S2 are less homogeneously distributed compared to those in sample S1. This should be related to the different preparation techniques used for both samples. Therefore, in some minor regions of crystal S2 with a sufficiently high local defect concentration, also magnetic clusters are formed with decreasing $T$. We suppose that these clusters are responsible for the flattening of $\chi(T)$ below 100 K. On the other hand,
we suggest that a predominant part of magnetic clusters leads to the formation of a Griffiths (G) phase \[23\,28\]. Hence, we ascribe the observed anomalous power-law of the susceptibility at low \( T < 30 \text{ K} \) to the formation of a Griffiths-phase:

\[
\chi(T) = \chi_0 + C_{\mu}C/T^{1-\lambda_\mu}, \tag{1}
\]

where \( \lambda_\mu \approx 0.67(3) \). At high \( T \), \( \chi(T) \) of sample S2 can be fitted by a Curie law \[23\] :

\[
\chi(T) = \chi_0 + C_{\mu}C/T, \tag{2}
\]

with the constant susceptibility \( \chi_0 = 4.4 \times 10^{-4} \text{emu/mol} \) and the Curie constant \( C_{\mu} = 0.115 \text{emu/mol-K} \). A fit of our data by Eqs. \[12\] is shown in Fig. 3(a) (a zoom for high-\( T \) is shown in the supplement (Fig. 3ap). The value of \( C_{\mu} \) provides direct insight into the defect concentration \( \delta \), if a microscopic model is adopted. We are enforced to adopt such a "point"-defect model, anyway, since no other minority phase could be detected so far \[27\]. For example, this value of \( C_{\mu} \) can be explained by about \( \delta_{\text{S2}} \sim 0.6 \text{ at.\% of Fe}^{+2} \) interstitials with an effective moment \( 5.4 \mu_B \). The susceptibility of sample S1 cannot be fitted by Eq. \[2\] at \( T < 300 \text{K} \). This suggests a stronger interaction between the LM which is probably related to a higher defect concentration \( \delta_{\text{S1}} \) in sample S1 compared to \( \delta_{\text{S2}} \) if the same microscopic model is adopted for both crystals. Note, that we do not expect that \( \delta_{\text{S1}} \) essentially exceeds \( \delta_{\text{S2}} \) since both samples have similar \( T_c \).

We show \( C(T)_p/T \) for both samples in Fig. 3. In case of a SG-phase the magnetic contribution \( C_m \) to the SH varies approximately linearly at \( T < T_f \) similar to the usual electronic contribution \( C_{el} \) in case of a FL \[24\,25\,29\]. Empirically, this behavior can be approximated by \( C_m \approx c_1T + c_2T^2 \), where \( c_1 \) and \( c_2 \) are constants. Then, the normal state SH of sample S1 can be described by:

\[
C_p(T) = (\gamma_{el} + c_1)T + c_2T^2 + \beta_3T^3 + \beta_5T^5. \tag{3}
\]

On the other hand, in case of a G-phase (sample S2), \( C(T)_G/T \propto \chi(T) \) \[23\,28\]. Hence, for the SH we have:

\[
C_p(T) = \gamma_{el}T + \gamma_GT^{\lambda_G} + \beta_3T^3 + \beta_5T^5, \tag{4}
\]

where \( \lambda_G \approx 0.67 \) according to our magnetic measurements. The data of our two crystals can be fitted by Eqs. \[33\] and \[33\] using the same lattice contribution \( \beta_3 = 0.68(2) \text{ mJ/mol-K}^4 \) and \( \beta_5 = 10^{-4}(0.5)\text{ mJ/mol-K}^6 \) with \( \gamma_{el} = 60(10)\text{ mJ/mol-K}^2 \), \( \gamma_G = 56(10)\text{ mJ/mol-K}^{1-\lambda_G} \), \( c_1 = 29(5)\text{ mJ/mol-K}^2 \) and \( c_2 = 2.6(5)\text{ mJ/mol-K}^3 \), respectively. Below 6 K the experimental data for crystal S2 deviate from the fitting curve (Fig. 3). This behavior is accompanied by kinks in the resistivity and the SH data (see inset Fig. 3(b) and Fig. 3). It seems that \( \rho(T) \) approaches a FL-like behavior for \( T < 6.5 \text{ K} \). At \( T_m \sim 4 \text{ K} \), slightly above \( T_c \), another magnetic anomaly is well visible in the SH data. In analogy with \[30\] we attribute the observed behavior for crystal S2 to a freezing of the G-phase and the formation of a cluster glass (CG) phase. Note that in case of metallic SG \[24\,31\] a large magnetic contribution to SH is expected. For example, AuFe SG \[29\] with 1 at. \% of Fe has a magnetic contribution \( C_F^{el}/T=3.3-4.6\text{ mJ/K}^2\text{g-at.} \) at \( T = 0 \). Assuming that \( C_m/T \) at \( T = 0 \) is nearly independent of the LM concentration \[25\,31\], we arrive at \( c_1 \sim ZC_F^{el}/T = 17-23\text{ mJ/mol-K}^2 \) in the case of sample S1 (with \( Z=5 \) atoms per f.u.) in accord with our findings. Remarkably, our findings are in a semi-quantitative agreement with the ’universal’ Overhauser relation \[25\] (obtained in the low \( T \)-approximation) rewritten in our notation

\[
c_1T_f = \frac{\pi^2}{9} \frac{S(S+1)}{2S+1} N_A k_B Z\delta_{\text{S1}}, \tag{5}
\]

where \( N_A \) is the Avogadro’s number. From Eq. \[6\] we have \( \delta_{\text{S1}} \approx 2 \text{ at.\% for Fe}^{+2} (S = 2) \). Then we may propose a realistic microscopic scenario for excess Fe induced spin-glasses with incommensurate short-range order. Hence, the observed additional \( C_m \) due to SG phase naturally explains variations and even very high nominal values of \( \gamma_m > 90 \text{ mJ/mol-K}^2 \) reported recently \[12\,13\,19\].

The presence of disordered magnetic phases inevitably leads to deviations from the FLB for \( \rho(T) \) \[24\]. In case of a SG-phase the NLB shows up for \( \rho \) in the anomalous exponent \( \alpha \approx 1.5 \) \[32\]. However, this value differs from our observed value \( \alpha = 1.77 \) for crystal S1 (Fig. 1(b)). For the G-phase, \( \alpha \leq 1.5 \) is suggested by most of the experimental data \[23\]. This is far from the effective value \( \alpha = 1.76 \) for crystal S2. We ascribe this puzzle to multi-band effects, if the impurity scattering dominates only in a part of the Fermi surface (FS). In fact, for the sake of simplicity, we consider two parallel channels with different \( \rho(T) \)-laws (see also the supplement). As shown in Fig. 1(b), our data are well fitted, if for one part of the Fermi surface NFLB is assumed with \( \rho_m(T) = \rho_{m0} + A_mT^\alpha \) and \( \alpha = 1.5 \) (sample S1) or \( \alpha = 1 \) (sample S2) whereas for the remaining parts the standard FLB holds: \( \rho_m(T) = \rho_{m0} + A_mT^2 \). In this case for the \( T \)-dependence of the effective resis-
tivity we have:

\[
\rho_{\text{eff}}(T) = \rho_m(T) \left[ 1 + \frac{\rho_n(T)}{\rho_0(T)} \right]^{-1}.
\] (6)

Thus, the obtained value of \( \gamma_{cl}=60(10)\text{mJ/mol-K}^2 \) might be considered as a new representative intrinsic value for a perfectly clean K122 system without LM. Such a value is strongly supported by the observation of a large residual contribution \( \gamma_r \approx 15 \text{mJ/mol-K}^2 \) (extrapolated to \( T = 0 \)) which amounts about 60% of the linear contribution \( \gamma_1 \) of the spin-glass (SG) above \( T_c \). In other words, the SG is somewhat suppressed at low \( T \) where the superconductivity is most dominant [1]. Moreover, independent theoretical estimates, including also a Kadowaki-Woods analysis, yield similar values of \( \gamma_{el} \) [9]. Following the analysis given there, we are left with an el-spin fluctuation coupling constant of \( \lambda_{el} \approx 1 \). We note that similar residual contributions have been observed also for other pnictides and chalcogenides and are often ascribed to spatial phase separation but a superconducting and a magnetic region [3]. Such a scenario can be excluded for our samples which show no secondary phases. The obtained value of \( \gamma_{cl} \) allows us to re-estimate \( \Delta C_{el}/\gamma_{el}T_c \) which amounts now 0.8(2) using \( \Delta C_{el}/T_c \approx 50 \text{mJ/mol-K}^2 \). Note, that this \( \text{new } \Delta C_{el}/\gamma_{el}T_c \) value is close to the predictions for \( d \)-wave or \( p \)-wave pairing [3]. Hence, to clarify the symmetry and the nodal structure of the SC order parameter, a careful sample characterization with respect to the presence of defect induced LM might be important for K122 and other Fe-pnictides. Naturally, the observed jump values don’t fit the strong pair-breaking relation \( \Delta C_{el} \propto T_c^3 \) [36]. To the best of our knowledge, K122 is a rare case for 122 superconductors not to fit to this ”universal” relation. We attribute the weak pair-breaking in K122 to magnetic intraband/or scattering between parts of FSs with the same sign of the order parameter provided by the SG and to the nearly absence of pair-breaking due to nonmagnetic impurities for scattering in between gap regions of different signs for intraband and interband scattering as well suggested by the unusually low residual resistivity \( \rho_0 \) of our samples. Another important fact is that in K122 with a SG phase no Pauli limiting for the upper critical field has been observed [19] in contrast to La-1111 samples where LM cause a sizable Pauli limiting effect [10]. This might indicate that the freezing of the SG reduces the polarization effect for itinerant electrons from the LM compared to a paramagnetic state. In general, the study of how superconductivity is affected by a SG like state and vice versa is a challenging issue in the framework of the old problem of coexisting magnetism and superconductivity not studied in detail since it has been observed in few cases, only, e.g. (Lu,Gd)Ni$_2$B$_2$C [32], UPt$_3$ [23,37]. (Note, that in case of Fe$_{1+y}$(Te$_{1-x}$Se$_x$) for \( y \ll 1 \) and \( x \approx 0.2-0.4 \), a SG phase in between an AFM region and a superconducting one has been detected recently by neutron scattering [38]. Anyhow, a better understanding of this interplay can be helpful for a deeper insight into these glassy states being in the focus of modern solid state physics including the interplay of disorder and quantum criticality [23,39].

To summarize, analyzing low-\( T \) transport and thermodynamic data we found that in K122 disordered magnetic phases (Griffith and spin glass-like) may occur near superconductivity and even coexist with it, especially if not all electrons are strongly affected by the glassy magnetic subsystem. Our data indicate that excess Fe provides the corresponding local magnetic moments (LM). The observed deviations from the standard Fermi-liquid behavior in the resistivity, the unusual large magnetization, the anomalously large value of the nominal Sommerfeld coefficient \( \gamma_c \) and the small value of \( \Delta C_{el}/\gamma_{el}T_c \) are ascribed to the coexisting disordered magnetic phases. The observed deviation from \( \Delta C_{el} \propto T_c^3 \) behavior suggests a weak pair-breaking due to the LM. To confirm the proposed above microscopic nature of the LM, the glass- and the coexisting magnetic phases sizable effects from the presence of a very small LM concentration is expected. This might explain e.g. the rather different superconducting properties even for different parts of the same single crystal [40].

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Details of the resistivity fit

The Fermi surface of K122 consists of 4 sheets with comparable partial densities of state (DOS) \[8\]. To specify our model, we suppose that the scattering by magnetic impurities becomes dominant only for one of these 4 FS, whereas the remaining 3 are almost unaffected. This way FLB is conserved there. Taking into account that the sample with a slightly higher value of RRR \( RRR_5 \approx 480 \) shows FLB with \( \rho_{FL0} \approx 0.47 \mu \Omega \text{cm} \) and \( A_{FL} = 0.030(7) \mu \Omega \text{ cm/K}^2 \).

FIG. 4: ap (Color) \( T \)-dependence of the molar susceptibility of sample S2 at \( B//ab = 1 \) and high \( T \). The interval in between 220-300 K has been used for the fit according to Eq. \[2\] given in the main text.
and assuming nearly equal contribution of each sheets to $\rho$ we adopted for $\rho_n(T)=4/3\rho_F L(T)$. The best fit from 5.5 to 15 K with this $\rho_n$ gives for $\rho_{m0} = 14.4 \mu\Omega\text{cm}$, $A_m = 0.358 \mu\Omega\text{cm/K}^{1.5}$ for S1 crystal and $\rho_{m0} = 3.93 \mu\Omega\text{cm}$, $A_m = 2.3 \mu\Omega\text{cm/K}$ for crystal S2, respectively. The essentially, higher value of $\rho_{m0}$ for S1 is consistent with the higher amount of magnetic defects as estimated from our susceptibility data.