Interplay between conducting and magnetic systems in the antiferromagnetic organic superconductor $\kappa$-(BETS)$_2$FeBr$_4$

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The mutual influence of the conduction electron system provided by organic donor layers and magnetic system localized in insulating layers of the molecular charge transfer salt $\kappa$-(BETS)$_2$FeBr$_4$ has been studied. It is demonstrated that besides the high-field re-entrant superconducting state, the interaction between the two systems plays important role for the low-field superconductivity. The coupling of normal-state charge carriers to the magnetic system is reflected in magnetic quantum oscillations and can be evaluated based on the angle-dependent beating behaviour of the oscillations. On the other hand, the conduction electrons have their impact on the magnetic system, which is revealed through the pressure-induced changes of the magnetic phase diagram of the material.

INTRODUCTION

Thanks to high crystal quality, relatively simple conduction band structures, and very good tunability between various electronic states, organic charge transfer salts can often serve as model systems for studying correlated electron physics, see, e.g., 1 for a review. In particular, the family of bis(ethylenedithio)tetraselenfulvalene (BETS) salts containing transition-metal ions like Fe$^{3+}$, Mn$^{2+}$, Cu$^{2+}$, etc. represents perfect natural nanostructures with alternating single-molecular conducting and magnetic layers. The charge transport in such compounds is provided by delocalized $\pi$-electrons of fractionally charged BETS donors, whereas magnetic properties are dominated by localized $d$-electron spins in the insulating anionic layers. While the latter usually undergo antiferromagnetic (AF) ordering at low temperatures, the ground state of the $\pi$-electron system is determined by a subtle balance between different instabilities of the normal metallic state and is particularly sensitive to the interlayer $\pi$-$d$ exchange interaction 2.

In the best-studied member of this family, $\lambda$-(BETS)$_2$-$\text{FeCl}_4$, the low-temperature metal-insulator transition is triggered by the AF ordering in the anionic layers 3. Moreover, at high magnetic fields where the AF insulating state is suppressed 8, the $\pi$-$d$ interaction leads, via the Jaccarino-Peter compensation effect 4 to a fascinating field-induced superconducting (SC) state 7. In the $\kappa$-(BETS)$_2$FeX$_4$ ($M = \text{Cl}, \text{Br}$) salts, differing from the former by the structure of the BETS layers, the $\pi$-$d$ interaction is weaker. As a result, they preserve metallic properties and even become SC below the Néel temperature 10. However, the magnetic interactions remain very important, as seen, for instance, in the high-field re-entrant superconductivity in the X = Br salt 7,8.

In this paper we show a few examples illustrating the entanglement of the magnetic and conducting systems in $\kappa$-(BETS)$_2$FeBr$_4$. In Sec. 4 we present data on the low-temperature phase diagram at ambient pressure as well as under high quasi-hydrostatic pressure. In addition to already known effects, we report on some new results revealing the influence of the magnetic system on the ground state of conduction electrons and vice versa. In Sec. 5 magnetoresistance quantum oscillations are presented. Here we focus on the effect of the Zeeman splitting on the oscillation behaviour, which provides quantitative information on the strength of the $\pi$-$d$ coupling, but also shows some unexpected features.

EXPERIMENTAL

Crystals of $\kappa$-(BETS)$_2$FeBr$_4$ were grown electrochemically 9 and had the form of rhombic platelets of submillimeter size and the largest surface parallel to the conducting BETS layers, that is the crystallographic ac-plane. The interlayer (|| $b$-axis) resistance was measured by standard 4-terminal a.c. technique using a low-frequency lock-in amplifier. High-pressure measurements were done in a Be-Cu piston-cylinder clamp cell with a silicon-organic liquid GKZh as pressure medium. The room- and low-$T$ pressure values were evaluated from the resistance of a calibrated manganin coil. Magnetoresistance measurements were done at ambient pressure in magnetic fields up to 14 T. The samples were mounted on a holder allowing in-situ rotation of the sample around an axis perpendicular to the external field direction. The orientation of the crystal was defined by a polar angle $\theta$ between the field and the crystallographic $b$-axis (normal to conducting layers).

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Low-field superconductivity protected by AF ordering

The low-field SC transition is also affected by the $\pi$-$d$ interaction. As the applied field increases from zero, the resistance gradually increases, indicating that the material is in the resistive flux-flow regime. However, at a certain field a sharp jump to the normal-state resistance value is observed. Most clearly it is seen in the 0.5 and 0.6 K curves in Fig. 4. This jump has been associated with a transition of the Fe spin system from the AF to a paramagnetic (PM) state. Since the external field $B$ is applied along the easy axis, the Fe spins are aligned alternately parallel and antiparallel to $B$. Thus, the average exchange field on the $\pi$-electron spins is zero. The total effective field $B_{\text{eff}} = B + B_J$ is simply equal to the applied field, which is not strong enough to kill superconductivity. As soon as, as the AF order is broken, the majority of Fe spins turns parallel to $B$, creating a strong exchange field $B_J \approx -10$ T. Therefore the effective field on $\pi$ spins sharply increases, causing a destruction of superconductivity by the Pauli paramagnetic pair-breaking mechanism.

The described scenario explains simultaneous suppression of the AF order in the magnetic system and of the SC order in the conducting system. However, Konoike et al. have reported resistive and magnetic torque data suggesting that the two transitions, while being close to each other, do not exactly coincide, at least at the lowest temperatures. A possible explanation is that at low temperatures the AF state undergoes a spin-flop transition before being completely destroyed by magnetic field. If so, the Fe spins acquire a finite average component in the field direction. If this component is strong enough, it creates an exchange field sufficient to suppress superconductivity in the BETS layers.

PHASE DIAGRAM

High-field re-entrant superconductivity

The coupling between the magnetic and conduction systems is most evidently manifested in the SC properties of $\kappa$-(BETS)$_2$FeBr$_4$. In Fig. 4 we plot examples of interlayer resistance traces in a magnetic field aligned in the conducting layers, parallel to the crystallographic $a$-axis. This direction coincides with the easy magnetization axis of the $d$-electron spins. Two SC regions are clearly seen, one below $\sim 2$ T and the other at high fields, $\geq 9.5$ T at the lowest temperature. The latter is known as field-induced or, here maybe better, re-entrant superconductivity. While in the present data the resistance does not completely vanish, a full re-entrant SC transition has been observed at lower temperatures, $T < 0.3$ K. From the position of the center of the SC dip one can estimate the effective exchange field imposed on the condution $\pi$-electron spins by the localized $d$-electron spins aligned in the field direction, $B_J \approx -12.6$ T (the $"-$ sign indicates the AF interaction), in perfect agreement with the earlier reports. This corresponds to the exchange coupling energy $J_{\pi d} = \mu_B g B_J / S_d \approx 0.9$ meV, where we plugged in the Fe$^{3+}$ electron spin $S_d = 5/2$ and assumed the $g$-factor equal to 2.0 ($\mu_B$ is the Bohr magneton). This value is quite small; nevertheless, as we see, this interaction has a strong impact on the electronic state.

FIG. 1: Interlayer resistance $R_\perp(T)$ of $\kappa$-(BETS)$_2$FeBr$_4$ as a function of magnetic field applied parallel to the inplane $a$-axis, which is the easy magnetization axis in this system. Low-field (below 2 T) and high-field ($B > 9.5$ T) SC regions are clearly seen. The inset shows the low-field region in a larger scale.
phase occupies a significant part of the ambient-pressure phase diagram \cite{14}. The difference stems from different relative contributions of the direct \(d\!-\!d\) exchange and indirect RKKY exchange, involving the \(\pi\!-\!d\) and \(\pi\!-\!\pi\) coupling, in setting the AF order. In \(\kappa\!-(\text{BETS})_2\text{FeBr}_4\) the ordering is predicted to be strongly dominated by the direct exchange, whereas in the \(\kappa\!-\!\text{Cl}\) salt the indirect interactions play a considerable role \cite{15}. The delocalized \(\pi\)-electrons provide much more isotropic interactions in the plane of conducting layers than the \(d\)-electrons localized in the insulating layers. Therefore the magnetic anisotropy of the \(\kappa\!-\!\text{Cl}\) salt is weaker, favouring a spin-flop from the easy \(a\)-axis to the next-easy inplane \(c\)-axis at \(B\!\parallel a\). Turning to our salt, we can speculate that high pressure leads to a stronger enhancement of the indirect exchange, thus facilitating the spin flop transition and making the CAF phase more stable. This looks reasonable, since the conduction electrons in organic metals are known to be extremely sensitive to pressure \cite{12}.

**Magnetic Quantum Oscillations**

The influence of the magnetic system on the normal-state charge carriers can be probed by magnetic quantum oscillations. Fig. 3 shows an example of oscillating resistance (Shubnikov-de Haas, SdH oscillations) in a field perpendicular to conducting layers, \(B\!\parallel b\). The AF ordering is reflected in the behaviour of the oscillations as well as in the nonoscillating magnetoresistance component. In Fig. 3 one can distinguish two different magnetoresistance regimes corresponding to the AF (\(B \leq 5\,T\)) and PM (\(B > 5\,T\)) states, respectively, in agreement with earlier findings \cite{17,18}. The SdH oscillations also differ drastically in these two regimes. In the PM state the oscillations originate from the classical \(\alpha\) and magnetic-breakdown (MB) \(\beta\) orbits on the Fermi surface predicted by the tight-binding band structure calculations \cite{9}, see Fig. 3(b). In Fig. 3(c) we show the fast Fourier transform (FFT) spectrum consisting of the fundamental harmonics, \(F_\alpha = 847\,T\) and \(F_\beta = 4230\,T\), and their combinations \cite{17,18}. By contrast, in the AF state only low-frequency oscillations, \(F_\beta \approx 62\,T\), are observed, indicating a Fermi surface reconstruction caused by the ordering \cite{18}.

Moreover, even in the high-field PM state the SdH oscillations are affected by the \(\pi\!-\!d\) coupling, providing a basis for its quantitative evaluation. In usual metals without magnetic interactions, the Zeeman splitting leads to a phase shift between oscillations corresponding to spins parallel and antiparallel to the applied field. This gives rise to a field-independent spin damping factor \cite{16}, which in the case of a strongly anisotropic layered metal has the form: \(R_s = \cos(\frac{g}{2}m^*\alpha/\cos\theta)\), where \(g\) is the Landé \(g\)-factor, \(\theta\) is the angle between the magnetic field and the normal to conducting layers (in our case the \(b\)-axis), and \(m^*_s = m^*(\theta = 0)\) the relevant cyclotron

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**Pressure effect**

Fig. 2 also shows the phase diagram obtained under hydrostatic pressure, \(p = 4.5\,\text{kbar}\). Superconductivity is rapidly suppressed by pressure, which is usual for organic superconductors \cite{12}. According to Otsuka et al. \cite{13}, the critical pressure for superconductivity is 4\,kbar. In our measurements already at 2\,kbar no trace of a SC transition has been found down to 0.42\,K.

By contrast to superconductivity, the AF ordering is enhanced under pressure. The zero-field Néel temperature increases by 25\% from the ambient pressure value, qualitatively in agreement with the earlier report \cite{13}. This is obviously caused by an enhancement of the exchange interactions due to compression of the crystal lattice.

In addition to the kink feature around 2\,T, a clear second feature has been detected in the \(B\)-dependent resistance at \(T \leq 1.5\,\text{K}\). The positions of both kinks are plotted in Fig. 2 (squares). The behaviour resembles that observed on the isostructural sister compound \(\kappa\!-(\text{BETS})_2\text{FeCl}_4\) (\(\kappa\!-\!\text{Cl}\) salt) at ambient pressure \cite{14}. In the \(\kappa\!-\!\text{Cl}\) salt this behavior was associated with a spin-flop transition into an intermediate, CAF state. Therefore, we suggest that the same happens in the present \(\kappa\!-(\text{BETS})_2\text{FeBr}_4\) salt under pressure.

Comparing to the present compound, in \(\kappa\!-\!\text{Cl}\) the CAF

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**FIG. 2:** Phase diagram of \(\kappa\!-(\text{BETS})_2\text{FeBr}_4\) in magnetic field parallel to the easy axis. Circles and stars correspond to the AF and SC transitions, respectively, recorded at zero pressure. The hollow symbols have been plotted according to Konoike et al. \cite{8}. Squares show the transition points taken from temperature (hollow symbols) and field (solid symbols) sweeps at \(p = 4.5\,\text{kbar}\). The lines are guides to the eye.
dependent on the conduction electrons, the spin factor becomes field dependent \([9]\) and magnetic-breakdown \((\beta)\) orbits are shown. (c) FFT spectrum of the SdH oscillations in the field window 9 to 14 T. (d) Amplitude of the oscillations plotted against inverse field. The dashed line is the best fit using the standard theory \([17\text{–}19]\), no splitting has been reported for the \(\alpha\)-peak in the SdH spectrum reproducibly shows splitting \([21\text{–}23]\). Indeed, the beat frequency, \(F_b\), is plotted against inverse field, \(T_D = 0.25 \pm 0.3\) K.

In Fig. 3(c) the FFT peaks containing the MB frequency \(F_\beta\) are split. Cépas et al. \([21]\) were the first to suggest that the splitting \(\Delta F_\beta \approx 100\) T comes from beating caused by the field-dependent spin factor in Eq. \([14]\). Indeed, the beat frequency, \(F_b = \Delta F_\beta / 2\), yields a reasonable value of the exchange field, \(|B_\alpha| = 12.5\) T, if we substitute \(g = 2.0\), \(m^*_\alpha = 8.0\) \([17]\) and \(\cos \theta = 1\) (as \(B \perp\) layers). The problem, however, is that while the \(\beta\)-peak in the SdH spectrum reproducibly shows splitting \([17\text{–}19]\), no splitting has been reported for the \(\beta\)-oscillations. In our measurements no sign of modulation of the \(\alpha\)-oscillation amplitude has been found in the field window 5.5 to 14 T. This can bee seen from Fig. 3(d) where the amplitude \(A_\alpha\) is plotted against inverse field, revealing a monotonic exponential dependence. Fitting it with the standard formula for the field-dependent oscillation amplitude yields the Dingle temperature (a quantity characterizing the scattering rate, \(k_B T_D = h/2\pi\tau\)) \(T_D = 0.25 \pm 0.3\) K. According to Eq. \([29]\), the absence of a minimum in the oscillation amplitude in the interval between 5.5 and 14 T would correspond to the exchange field being smaller than 0.9 T (the cyclotron mass \(m^*_\alpha = 5\) \([17\text{–}18]\) was used for the estimation). This controversy calls for a more thorough investigation of the effect of magnetic interactions on the SdH oscillations.

To this end we have carried out experiments at different orientations of magnetic field. Figure 4 shows the \(\beta\)-oscillating component of magnetoresistance measured at different polar angles \(\theta\). One clearly sees beats with the maxima and minima of the oscillation amplitude changing with \(\theta\). Considering the beats as coming from the field-dependent spin factor, the first, obvious feature following from Eq. \([10]\) is that for \(B = |B_\beta|\) the oscillation amplitude must always be at maximum, independently of the angle. For \(\theta \geq 20^\circ\) the behaviour is consistent with Eq. \([11]\), showing the \(\theta\)-independent maximum position at \(B \approx 13\) T. However, for small tilt angles, \(-20^\circ < \theta < 20^\circ\), the beats become more complex. Not only some of the beat nodes become much less pronounced but also their positions shift in an apparently irregular manner. For example, at \(\theta \approx \pm 9^\circ\) a minimum in the amplitude is found.
around 13 T, the field where the main (θ-independent) maximum should be expected.

Using the condition for zeros of the spin factor $R_\alpha$ determined by Eq. (1), one can fit the positions of the amplitude minima/nodes with the exchange field and $g$-factor as fitting parameters. The results of such fitting are shown in Fig. 5. In line with what was qualitatively described above, at $|\theta| \geq 20^\circ$ the obtained values, $B_J = -13.0 \pm 0.1$ T and $g = 2.0 \pm 0.05$, are very reasonable and consistent with the estimation based on the position of the re-entrant superconductivity region of the phase diagram, see Sec. 5. At lower tilt angles both fitting parameters strongly deviate from these values. At present we do not have a satisfactory explanation of this anomalous behaviour. One might appeal to other possible mechanisms of beating of the SdH oscillations have to be taken in consideration, such as weak warping of the Fermi surface in the interlayer direction [22] or mosaicity of the crystal.

As noted above, the $\alpha$-oscillations corresponding to the smaller, classical orbit in Fig. 3(b) should also be modulated by the field-dependent spin factor. However, we have found no modulation at tilt angles below 15-20°, i.e. in the range where the beat behaviour of the $\beta$-oscillations is also anomalous. In Fig. 4 we show the evolution of the $\alpha$-oscillating component at $\theta \geq 20^\circ$. The weak modulation observed at 20° develops gradually into full beating with periodic nodes. However, the node positions are still inconsistent with those found on the $\beta$-oscillations. As shown in Fig. 4, apparently only every second expected node shows up in the experiment. According to Eq. (1), this would imply that the $g$-factor on the $\alpha$ orbit is only one half of that on the $\beta$ orbit. This would be highly surprising, especially since the latter does incorporate the $\alpha$ orbit as a part. Thus, further angle-resolved studies are needed to clarify the situation.

Perhaps low-$T$ ESR measurements will give a clue to the puzzle.

**SUMMARY**

The localized $d$-electron spins of Fe$^{3+}$ ions, responsible for magnetic properties, and itinerant electrons originating from the $\pi$ orbitals of BETS molecules are spatially separated in the layered organic metal $\kappa$-(BETS)$_2$-FeBr$_4$. The exchange interaction between the two systems is weak, $J_{\pi d} \leq 1$ meV. Nevertheless this interaction has strong impact on the electronic properties.

The role of $\pi$-$d$ interaction is very clearly manifested in the high-field re-entrance superconductivity [23], but also in the low-field superconductivity, which turns out to be "protected" by the AF ordering and disappear simultaneously with the latter at low temperatures. In the normal state, the $\pi$-$d$ coupling is reflected in the angle-dependent beating behaviour of magnetic quantum oscillations. At sufficiently strongly tilted field, $|\theta| \geq 20^\circ$, the beats of the magnetic-breakdown $\beta$-oscillations can be quantitatively accounted for by including the exchange field $B_J = -13$ T in the spin damping factor $R_\alpha$ for the oscillation amplitude. However, at lower tilt angles the beat positions are surprisingly shifted, resulting in an apparently strong changes in both $B_J$ and the $g$-factor. This anomaly as well as the unexpected difference between the beats of the $\beta$- and $\alpha$-oscillations require further investigation.

Finally, the conduction system in its turn seems to
influence the magnetic ordering of the d-electron spins through the indirect RKKY exchange. This is reflected in the change of the shape of the phase diagram and appearance of the spin-flopped AF phase under pressure. It would be nice to perform magnetic measurements under pressure in order to determine the exact nature of the high-field AF phase.

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