

## Magnetism and fermiology of $\kappa$ -(BEDT-TSF) $_2$ FeCl $_4$

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Magnetization studies reveal that the ground state of  $\kappa$ -(BEDT-TSF) $_2$ FeCl $_4$  is  $J = 1/2$  with weak antiferromagnetic correlations. Quantum oscillation studies indicate that the effective masses of the quasiparticles are considerably enhanced with respect to those of isostructural  $\kappa$ -(BEDT-TSF) $_2$ GaCl $_4$ . We attribute the mass enhancement to spin fluctuation effects involving the Fe magnetic moments within the inorganic layer. [S0163-1829(98)00615-8]

There has been a growing interest in the synthesis of charge-transfer salts containing magnetic anions, so as to investigate their possible influence on the ground-state properties of quasi-two-dimensional systems. FeCl $_4^-$  is one such example that features in a number of salts.<sup>1-3</sup> Although most of these salts are Mott insulators,<sup>1,2</sup> (BEDT-TSF) $_2$ FeCl $_4$  [where BEDT-TSF stands for bis-(ethylenedithio)tetraselenafulvalene] crystallizes in two novel metallic phases:<sup>3</sup> a  $\kappa$  phase that remains metallic to the lowest temperatures and a  $\lambda$  phase that undergoes a metal-insulator transition at  $T_{MI} = 8$  K. These strikingly different behaviors occur even though the  $\kappa$  and  $\lambda$  phases represent only different crystallographic morphologies of the same salt. The condensation of carriers in the low-temperature insulating ground state of the  $\lambda$  phase salt is thought to be assisted by antiferromagnetic interactions of the Fe<sup>3+</sup> moments.<sup>4</sup>

One way of assessing the influence of the magnetic anions on the ground-state properties is to draw comparisons with the  $\kappa$  and  $\lambda$  phase salts in which the FeCl $_4^-$  anion has been substituted with nonmagnetic GaCl $_4^-$ .<sup>5-7</sup> As yet another example of the close interplay between antiferromagnetism and superconductivity,  $\lambda$ -(BEDT-TSF) $_2$ GaCl $_4$  transforms to a superconducting ground state below  $T_c \approx 4.35$  K.<sup>6,7</sup> The nature of the interactions between electrons and other entities in the system, such as magnetic ions, may be discernible from studies of the quantum oscillatory effects,<sup>8-10</sup> although measurements of the quantum oscillatory phenomena have been somewhat incomplete in this series of salts.<sup>11-13</sup>

In pursuit of a better understanding of the mechanisms responsible for the ground-state properties of the (BEDT-TSF) $_2$ FeCl $_4$  salts, we report measurements of the magnetization of the  $\kappa$  phase salt at low fields as well as the de Haas-van Alphen (dHvA) and Shubnikov-de Haas (SdH) oscillations at higher magnetic fields. In contrast to the  $\lambda$  phase salt,<sup>14,15</sup>  $\kappa$ -(BEDT-TSF) $_2$ FeCl $_4$  behaves as a  $J = 1/2$  paramagnet (where  $J$  refers to the total angular momentum) with additional evidence for weak antiferromagnetic interac-

tions, characterized by a Curie-Weiss temperature of  $\Theta_p \approx -1.5$  K. The lower spin state together with weaker antiferromagnetic interactions are likely to play an important role in the mechanisms that predispose the  $\kappa$  phase to retain a metallic state at low temperatures. A comparison of the temperature dependence of the oscillations with that observed in the isostructural  $\kappa$ -(BEDT-TSF) $_2$ GaCl $_4$  analog<sup>12</sup> reveals that the quasiparticle effective masses in  $\kappa$ -(BEDT-TSF) $_2$ FeCl $_4$  are considerably enhanced. Although the extent of correlations appears to be weaker in the  $\kappa$  phase FeCl $_4^-$  salt, the enhancement of the effective mass suggests the existence of spin fluctuations (electron-paramagnon interactions) at low temperatures and high magnetic fields.

Single crystals in the form of thin platelets of volume  $\approx 1 \times 1 \times 0.1$  mm<sup>3</sup> were synthesized electrochemically on platinum electrodes<sup>16</sup> at a constant current of  $2 \times 10^{-3}$  Am<sup>-2</sup>, using 5.2 mg of BEDT-TSF and 440.1 mg of tetrabutylammonium tetrachloroferrate in 5 ml and 10 ml of 95% 1,1,2-trichloroethane: 5% ethanol (v/v), respectively. The reaction was carried out at 50.0 °C under dry nitrogen in a vibration-isolated environment, and the crystals (2.9 mg total) were harvested after 6 days. Magnetization measurements at low magnetic fields were made using a SQUID magnetometer; whereas dHvA measurements were performed using a compensated arrangement of detection coils in pulsed magnetic fields extending to 50 T.<sup>17</sup> Magnetotransport measurements in fields of up to 60 T employed a radio frequency lock-in technique, with electrical contacts applied by means of graphite paint. In all experiments, temperatures between 400 mK and 4 K were achieved by pumping on <sup>3</sup>He and <sup>4</sup>He reservoirs.

A plot of the reciprocal magnetic moment  $1/m$  of the sample versus temperature  $T$  is shown in Fig. 1(a) for an applied magnetic field  $\mu_0 H$  of 0.1 T. Deviations from ideal Curie-Weiss behavior, in particular the kink at  $\approx 90$  K, suggest the occurrence of spin excitations to higher crystal-field-split levels at elevated temperatures. The profile of Fig. 1(a) is very similar to that of the spin susceptibility observed by means of electron spin resonance (ESR) studies.<sup>14</sup> In spite of

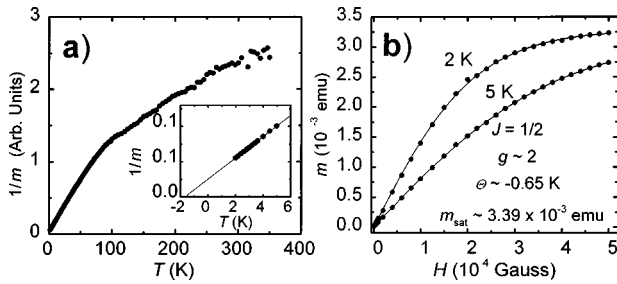


FIG. 1. (a) A plot of  $1/m$  vs temperature at 0.1 T. Antiferromagnetic correlations are indicated by the intercept of  $\Theta_p \approx -1.5$  K. (b) The magnetization vs magnetic field at  $T_N = 2$  and 5 K, with the fitting parameters shown for  $J = 1/2$ .

the nonlinearity at high temperatures, the existence of antiferromagnetic interactions is evident from the intercept at lower temperatures. A linear fit to the data below 5 K [see inset of Fig. 1(a)] yields  $\Theta_p = -1.5 \pm 0.1$  K, which is notably smaller than the intercept of  $-15$  K found for the  $\lambda$  phase salt.<sup>14</sup> As the magnetic field is increased, the total moment approaches saturation, as shown in Fig. 1(b) for  $T = 2$  and 5 K. Upon fitting these isothermal magnetization data to the Brillouin functions for  $J = 1/2, 3/2,$  and  $5/2$ , the lowest residuals, as well as the most physically meaningful fitting parameters [see Fig. 1(b)], are obtained for  $J = 1/2$ . The presence of antiferromagnetic interactions nevertheless requires  $T$  to be adjusted by a small amount  $\Theta_p$  to accommodate a Landé  $g$  factor of  $g \approx 2$ .<sup>14,15</sup> Further evidence supporting the  $J = 1/2$  result comes from a comparison of the absolute value of the saturated magnetic moment with that expected for a  $J = 1/2$  spin density of  $6 \times 10^{23}$  spins/mol (4 Fe ions per unit cell). The agreement is within  $\approx 30\%$ , given the sample volume of  $0.04 \pm 0.01$  mm<sup>3</sup> used in this study.

Since Hund's rules anticipate a  ${}^6S_{5/2}$  multiplet for triply ionized  $\text{Fe}^{3+}$ , the fitted value of  $J = 1/2$  is somewhat surprising. Although ESR studies provide evidence supporting the expected value of  $J = 5/2$  for the  $\lambda$ -(BEDT-TSF)<sub>2</sub>FeCl<sub>4</sub> salt, the results have been less certain for the  $\kappa$  phase salt. Kobayashi *et al.* originally quoted a value for the spin density consistent with  $J = 1/2$ ,<sup>14</sup> but later published a slightly higher value, which they proposed to be consistent with  $J = 5/2$  if partial screening of the incident microwaves by the conduction electrons is considered to account for the discrepancy.<sup>15</sup> Since the measurements of the magnetization probe the bulk of the sample directly, the value of  $J = 1/2$  determined for the  $\kappa$  phase salt obtained in this work can be considered with confidence. Nevertheless, the close similarity of the experimental curve of Fig. 1(a) to that of Ref. 14 suggests that the screening of the microwaves in Ref. 14 was not a significant factor. A likely reason for ambiguity in the two published results of Kobayashi *et al.* was the temperatures at which the spin densities were determined. While the spin density consistent with  $J = 1/2$  was obtained at low temperatures<sup>14</sup> (as is the case in this work), the larger estimate was obtained at room temperature.<sup>15</sup> The larger estimate more likely corresponds to a real increase of the spin density at elevated temperatures upon thermal activation of the moments to higher crystal-field-split spin states, as suggested by the kink at  $\approx 90$  K in Fig. 1(a). Interestingly, the

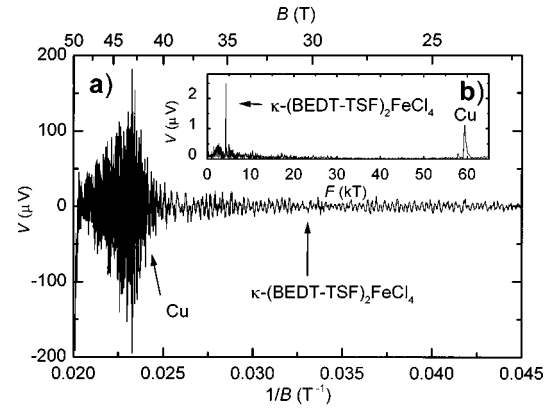


FIG. 2. (a) The measured dHvA voltage signal from  $\kappa$ -(BEDT-TSF)<sub>2</sub>FeCl<sub>4</sub> on the falling magnetic field at 450 mK after background subtraction. (b) Fourier transformation of the oscillations indicating a single spectral feature from  $\kappa$ -(BEDT-TSF)<sub>2</sub>FeCl<sub>4</sub> and others due to the polycrystalline Cu, which comprises the detection coils.

spin density obtained at room temperature<sup>15</sup> agrees precisely with what should be expected for  $J = 3/2$ .

The realization of a  $J = 1/2$  state in the  $\kappa$ -(BEDT-TSF)<sub>2</sub>FeCl<sub>4</sub> salt (at low temperatures) suggests that the crystal-field splitting is stronger than the spin-orbit coupling. This situation is uncommon for  $d$ -electron metals, although  $\text{Fe}^{3+}$  does not exist as a free ion in this salt, but is covalently bonded to 4 Cl atoms. A yet more intriguing observation is that the lowest-energy spin state is different for the two phases, and is likely to reflect differences in the degree to which the tetrahedral arrangement of the Cl atoms is distorted by the lattice.<sup>15</sup> The existence of a lower spin state in the  $\kappa$  phase salt may nevertheless account for the weaker antiferromagnetic correlations in this material as well as the persistence of the metallic ground state at low temperatures.

Whereas low-field magnetization studies enable the spin magnetization to be studied, the interactions between the magnetic moments and the carriers usually reflect themselves most significantly in the quasiparticle properties of the system. The dHvA effect [Fig. 2(a)] is valuable in this respect, since it is a thermodynamic function of the state of the Fermi liquid. In Fig. 2(b), Fourier transformation of the dHvA oscillations reveals that the spectrum is dominated by a fre-

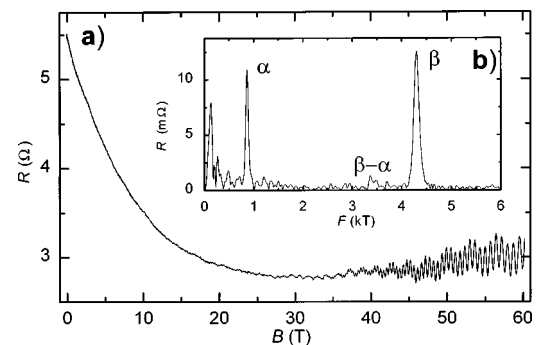


FIG. 3. (a) Magnetotransport measured in  $\kappa$ -(BEDT-TSF)<sub>2</sub>FeCl<sub>4</sub> in fields up to 60 T at 1.3 K. (b) Fourier transformation of the oscillations, yielding the  $\alpha$ ,  $\beta$  and  $\beta - \alpha$  frequencies characteristic of  $\kappa$  phase salts.

TABLE I. A comparison of the quantum oscillation frequencies and estimated effective masses obtained (where possible) from dHvA and SdH studies on  $\kappa$ -(BEDT-TSF)<sub>2</sub>FeCl<sub>4</sub> (this work) with those obtained for  $\kappa$ -(BEDT-TSF)<sub>2</sub>GaCl<sub>4</sub> by Tajima *et al.* (Ref. 12). Here,  $m_e$  represents the free-electron mass.

Orbit	FeCl <sub>4</sub> <sup>-</sup> anion $F, m^*$ (dHvA)	FeCl <sub>4</sub> <sup>-</sup> anion $F, m^*$ (SdH)	GaCl <sub>4</sub> <sup>-</sup> anion $F, m^*$ (SdH)
$\alpha$		$864 \pm 5$ T, $2.8 \pm 0.2m_e$	$816$ T, $1.2$ T $\pm 0.05m_e$
$\beta - \alpha$		$3354 \pm 20$ T	$3530$ T, $1.2 \pm 0.1m_e$
$\beta$	$4295 \pm 8$ T, $5.2 \pm 0.3m_e$	$4296 \pm 5$ T, $5.3 \pm 0.4m_e$	$4350$ T, $2.4 \pm 0.05m_e$

quency of  $4295 \pm 8$  T. On the basis of a comparison with the band-structure calculations<sup>15</sup> and other  $\kappa$  phase salts,<sup>19</sup> it is evident that this frequency corresponds to the large  $\beta$  orbit that results from magnetic breakdown. A general requirement of Luttinger's theorem<sup>18</sup> is that the area of the  $\beta$  orbit should accommodate all of the carriers in the system. From estimates of the electron density, made using low-temperature crystallographic x-ray data (at  $T = 10$  K),<sup>15</sup> we obtain  $F_\beta \approx 4296$  T (for two electrons per unit cell), which agrees comfortably with the experimental results.

A general consequence of performing dHvA experiments in strong magnetic fields is that, above  $\approx 40$  T in some samples showing only weak oscillations, the signal becomes dominated by dHvA oscillations originating from the polycrystalline copper, which comprises the detection coils. Shubnikov-de Haas oscillations, on the other hand, have the advantage of becoming much larger as the magnetic field increases, as evident in Fig. 3(a). Spectral analysis of the SdH oscillations reveals additional peaks corresponding to the  $\alpha$  pocket of the calculated Fermi surface<sup>15</sup> and the Stark quantum interference "difference orbit"  $\beta - \alpha$  (Ref. 19) [Fig. 3(b)]. Thus, the Fermi-surface topology of the FeCl<sub>4</sub><sup>-</sup> salt is essentially the same as that of the GaCl<sub>4</sub><sup>-</sup> salt.<sup>12</sup> This should be expected given that the crystallographic parameters for the two salts differ by less than 0.1%.<sup>14</sup>

Although the Fermi-surface topologies of the two  $\kappa$  phase salts appear to be the same, studies of the temperature dependence of the oscillations reveal that the effective masses in the FeCl<sub>4</sub> salt are  $\approx 2.2$  times greater than those in the GaCl<sub>4</sub> salt.<sup>12</sup> Fitting results of the function  $X/\sinh X$  (where  $X = 14.69 m^*T/B$ ) to the temperature dependence of the oscillations are listed in Table I; note that the effective masses extracted from the dHvA and SdH oscillations agree. Because the magnetism of the Fe<sup>3+</sup> ions represents the only appreciable difference between the two salts, it seems clear that they are responsible for the mass enhancement. The electronic specific heat<sup>20</sup> and the quasiparticle effective masses<sup>10</sup> are often found to be enhanced in metals containing paramagnetic or ferromagnetic ions; Fe, Co, and Ni being

perhaps the most well known examples. In these materials, the mass enhancement is attributed to spin fluctuation effects.<sup>10,20</sup> In  $\kappa$ -(BEDT-TSF)<sub>2</sub>FeCl<sub>4</sub>, the magnetic moments are strictly localized, in contrast to the quasi-itinerant magnetism in heavy-fermion systems.<sup>9</sup>

A comparison of effective masses in the two salts enables us to gauge the strength of the electron-paramagnon interaction. The extent of the mass enhancement is surprising given the spatial separation between the conducting (BEDT-TSF)<sub>2</sub><sup>+</sup> cations and the FeCl<sub>4</sub><sup>-</sup> anions. Further evidence for interactions between the conduction electrons and the magnetic moments is provided by the pronounced negative magnetoresistance in Fig. 3(a) at low fields. In this case, the negative magnetoresistance, which appears to follow the functional form of an exponential decay to  $\approx 30$  T, represents the gradual suppression of scattering as the moments become aligned by the magnetic field.

To summarize, magnetization experiments reveal that  $\kappa$ -(BEDT-TSF)<sub>2</sub>FeCl<sub>4</sub> behaves as a  $J=1/2$  paramagnet at low temperatures with weak antiferromagnetic interactions characterized by paramagnetic Curie-Weiss temperature of  $\Theta_p \approx -1.5$  K. This contrasts with the  $\lambda$  phase salt for which  $J=5/2$ . The low spin state in the  $\kappa$  phase salt is likely to be an important factor in causing the persistence of a metallic state to low temperatures. Although antiferromagnetic interactions appear to be of lower strength compared to the  $\lambda$  phase salt, quantum oscillation experiments nevertheless reveal that the quasiparticle effective mass in  $\kappa$ -(BEDT-TSF)<sub>2</sub>FeCl<sub>4</sub> is considerably enhanced, most likely due to electron-paramagnon interactions. Of further interest will be the influence of Zeeman transitions on the metallic state at higher magnetic fields.

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