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Magnetic-field-induced superconductivity in layered organic molecular crystals with localized magnetic moments

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λ-$(BETS)_2FeCl_4$ undergoes transitions from an antiferromagnetic insulator to a metal and then to a superconductor as a magnetic field is increased. We use a Hubbard-Kondo model to clarify the role of the Fe^{3+} magnetic ions in these phase transitions. In the high-field regime, the magnetic field acting on the electron spins is compensated by the exchange field H_e due to the magnetic ions. We show how H_e can be extracted from the observed splitting of the Shubnikov–de Haas frequencies. We predict the field range for field-induced superconductivity in other materials.

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The discovery of magnetic-field-induced superconductivity[1] in the two-dimensional compound λ-$(BETS)_2FeCl_4$ [where BETS is bis(ethylenedithio)-tetraselenafulvalene] is an example of the rich phase diagrams of organic molecular crystals.[2] Whereas, previously, pressure or chemical substitution has been used to change the electronic properties of these organic materials, it is remarkable that this compound undergoes successive electronic phase transitions as the magnetic field is increased. Below a temperature of 8 K, λ-$(BETS)_2FeCl_4$ is an antiferromagnetic (AF) insulator.[3] As a magnetic field is applied, it undergoes a first-order transition to a metal at 11 T. Close to this field, the magnetic moments associated with the spin 5/2 of the Fe^{3+} ions undergo a transition to a polarized paramagnet. If the magnetic field is parallel to the layers, there is a transition to a superconductor at 20 T,[1] which is then destroyed above 42 T.[4] The magnetic ions are essential to this behavior, since the compound with nonmagnetic ions, λ-$(BETS)_2GaCl_4$, is, in contrast, a superconductor at zero field,[5] despite very similar crystal structures.[6]

In this Communication we focus on three questions: (i) Why does the inclusion of magnetic ions change the ground state from a superconductor to an insulator? (ii) Is the magnetic-field-induced superconductivity due to the the Jaccarino-Peter effect,[4,7] where the external field is compensated by an internal exchange field due to the magnetic ions? and (iii) Does the Jaccarino-Peter picture survive if one takes into account the spin fluctuations associated with the magnetic ions?

Recently, Ziman introduced a two-dimensional Hubbard-Kondo model in order to understand question (i).[3] The model takes into account the four conduction bands associated with layers of BETS molecules [four highest occupied molecular orbitals (HOMO) per unit cell], a Kondo coupling between the localized $S=5/2$ spins and the conduction electrons, and the Coulomb repulsion between two electrons on the same BETS molecule. Ziman found that for small electron-electron repulsion the periodic potential due to the magnetic ordering (found self-consistently) at low temperature opens energy gaps on the Fermi surface.[3] A magnetic field, by aligning the moments, destroys the periodic potential, restoring the Fermi surface. However, to suppress the entire Fermi surface, this needs a Kondo coupling, $J>6$ meV, which is larger than the estimates that we extract from experiment below. Moreover, the system seems to have quite a large electron-electron repulsion, as suggested by comparison with the κ-$(BEDT\text{-}TTF)_2X$ family.[8] In this case, we show first that the system without the magnetic ions may be close to a Mott transition. Then, the Kondo coupling with the magnetic ions can drive the system into the insulating phase in order to gain some magnetic energy. These two scenarios of the metal-insulator transition lead to different physical pictures [spin-density-wave (SDW) insulator versus Mott-insulator].

Question (ii) has to be carefully examined. Although, it is clear that the magnetic ions can in principle produce an exchange field H_e that can compensate the external field, it is desirable to know the precise magnitude of H_e. We show how to extract it from the observed magnetic oscillations.[9] This allows us to rule out alternative proposals such as spin-triplet superconductivity, field-induced dimensional crossovers, or superconductivity mediated by spin fluctuations in the local moments.

Previous estimates of J (and so H_e) involve considerable uncertainty. In the high-temperature metallic phase, the exchange leads to an Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between the localized spins, $J_0=J^2\chi(Q_{AF})$ where χ_{AF} is the electronic spin susceptibility at the wave vector of the AF correlations. The high-temperature magnetic susceptibility gives an estimate of $J_0\sim 0.2$ meV.[3] To obtain the coupling J from this approach, we need to know the electronic spin susceptibility $\chi(Q_{AF})$. Using the free-electron band structure, $\chi(Q_{AF})=80\ (\mathrm{eV})^{-1}$[13] gives $|J|=1.5$ meV. Hotta and Fukuyama[10] suggested that the Kondo coupling comes from superexchange processes leading to an *antiferromagnetic* coupling ($J>0$). They estimated $J\sim 1$ meV, using hopping integrals found from Hückel calculations and assuming a value of 2 eV for the splitting between the d orbital of the Fe^{3+} and HOMO orbitals.

Mott insulator. We first argue that the materials without the magnetic ions are close to a metal-insulator transition. From the experimental point of view, the effect of the anion in λ-$(BETS)_2GaBr_zCl_{4-z}$ is to drive the electronic system from a superconductor for $z<0.8$ to an insulator $z>0.8$.[11] As the crystal structure is very similar in both cases, this means

that a small change in the electronic parameters [estimated to be smaller than 5% (Ref. 12)] yields two different phases. *Hence, the electronic system without magnetic ions is close to a metal-insulator transition*. From the theoretical point of view, the λ-$(BETS)_2X$ and κ-$(BEDT\text{-}TTF)_2X$ compounds have very similar band structures: in these three-quarter filled systems, two bands are isolated from the two others by quite a large gap.[6] This can be interpreted as the separation between the bonding and antibonding orbitals on a dimer of molecules.[8] Projecting out the bonding orbital on each dimer, the system is thus effectively half-filled and reduces to a triangular lattice Hubbard model.[8] As the Fermi surface has poor nesting, it undergoes a metal-Mott insulator transition at finite U/t. Chemical pressure can change this ratio driving the system from a metal (or superconductor) to an insulator.[8] Replacing nonmagnetic Ga^{3+} by magnetic Fe^{3+}, the electronic parameters change even less.[10] Even though this could also, in principle, drive the system from a metal to an insulator, it can not explain why a magnetic field induces a first-order transition to the metallic phase.

We now show that the magnetic character of the ions is important to drive the system into the insulating phase. Projecting out the bonding orbitals from Ziman's model leads to a simpler twoband model, with Hamiltonian:

$$\mathcal{H}=\sum_{\mathbf{ij},\sigma} t_{\mathbf{ij}}(c^{\dagger}_{\mathbf{i},\sigma}c_{\mathbf{j},\sigma}+\text{h.c.})+U\sum_{\mathbf{i}} n_{\mathbf{i},\uparrow}n_{\mathbf{i},\downarrow}$$

$$+J\sum_{\mathbf{i}} \vec{S}_{\mathbf{i}}\cdot\vec{\sigma}_{\mathbf{i}}+g_a\mu_B H\sum_{\mathbf{i}} S^z_{\mathbf{i}}+g\mu_B H\sum_{\mathbf{i}} \sigma^z_{\mathbf{i}},$$

where $c^{\dagger}_{\mathbf{i}}$ creates a hole on the dimer at site $\mathbf{i}$. $\vec{S}_{\mathbf{i}}$ is a spin-S operator for the local moments. $\vec{\sigma}_{\mathbf{i}}\equiv\frac{1}{2}\Sigma_{\alpha,\beta}c^{\dagger}_{\mathbf{i}\alpha}\vec{\sigma}_{\alpha\beta}c_{\mathbf{i},\beta}$ (where $\vec{\sigma}$ denotes the three Pauli matrices) is the spin-1/2 operator for the hole on site $\mathbf{i}$. U and J are, respectively, the projected Hubbard repulsion and the Kondo coupling. $t_{\mathbf{ij}}$ is the tight-binding hopping integrals between dimers.[8] g_a and g are the g-factors of the local moments and itinerant electrons, respectively.

Let us take the two limits of small and large U of this model. (i) At small U and J small enough, the phase is metallic due to imperfect nesting.[3] The localized spins are subject to an RKKY interaction. Treating the local moment spins classically, the total energy is $E_{metal}-zJ^2\chi(Q_{AF})S^2$, where $z=2$ is the number of magnetic bonds. (ii) At large U, the system is a Mott insulator. The electrons are antiferromagnetically ordered because of the Anderson superexchange process. Subsequently, the Kondo coupling forces the $S=5/2$ moments to be antiferromagnetically ordered with respect to the localized electronic spins. The magnetic energy is $-\frac{1}{2}JS$ per site and the total energy of the AF Mott insulator (AFMI) is $E_{AFMI}-\frac{1}{2}JS$. The gain in magnetic energy is much larger in the Mott phase than in the metallic phase [$J^2\chi(Q_{AF})\sim J^2/E_F\ll J$, where E_F is the Fermi energy]. We now assume that the expressions of the magnetic energies are still valid for intermediate U. The energy $-\frac{1}{2}JS$ assumes that the localized electrons have a full spin-1/2 magnetic moment and are not in a spin-liquid state. This is not obvious for the intermediate regime. However, we note that in κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ a first-order transition has been observed from a Mott insulator with about half the full moment to a superconducting phase.[13,14] This picture is also consistent with a recent exact diagonalization study of the Hubbard model on a triangular lattice at half filling.[15] If for $J=0$, $E_{AFMI}>E_{metal}$ (the Ga compound is a metal) it is possible that $E_{AFMI}-\frac{1}{2}JS<E_{metal}-zJ^2\chi S^2$, provided that J is large enough or the difference between E_{AFMI} and E_{metal} is small enough. A similar argument applies to the energy of the superconducting phase because the RKKY interaction near Q_{AF} is not modified in the superconducting state.[16]

Destruction of the insulating phase by temperature. Above the Néel ordering temperature ($T_N\sim J_0$) for the local moments the metallic phase has entropy of order $\ln(2S+1)$. In contrast, the insulating phase with AF order has zero entropy. Hence, to zeroth order in J_0, the metal-insulator transition is first order and occurs at a temperature of $T_{MI}\sim[E_{metal}(J=0)-E_{AFMI}(J)]/\ln(6)$.

Destruction of the insulating phase by a magnetic field. We calculate the classical energies of the metallic and AFMI states as a function of the magnetic field. Doing this, we can neglect the electronic susceptibility because $J_0\ll t_1, 4t_1^2/U$. (i) *Metallic phase*. We restrict ourselves to spiral ordering such as $\vec{S}_i=[S\cos\alpha\cos(Q.R_i),S\cos\alpha\sin(Q.R_i),S\sin\alpha]$. The energy is, $E(H,\alpha)=E_{metal}-zJ_0S^2\cos 2\alpha-g_a\mu_BHS\sin\alpha$. Minimizing this with respect to α gives $E(H)=E_{metal}-zJ_0S^2-(g_a\mu_BH)^2/8zJ_0$ for $H<H_N\equiv 4zSJ_0/g_a\mu_B$ which is the critical field to align the spins, and $E(H)=E_{metal}+zJ_0S^2-g_a\mu_BHS$ for $H>H_N$. (ii) *Insulating phase*. The energy is $E(H,\alpha)=E_{AFMI}-\frac{1}{2}JS\cos\alpha-g_a\mu_BSH\sin\alpha$. The minimization gives $E(H)=E_{AFMI}-\frac{1}{2}JS\sqrt{1+(2g_a\mu_BH/J)^2}$. Provided that $E_{metal}+zJ_0S^2<E_{AFMI}$, as the field increases the energy of the metal crosses that of the insulator, leading to a first-order transition into the metallic phase.

Field-induced superconductivity. The argument for the Jaccarino-Peter mechanism[4,7] is as follows. If the system is sufficiently two dimensional, when a magnetic field is applied parallel to the layers, the orbital motion of the electrons is quenched. The upper critical field is then determined by the Pauli paramagnetic limit.[17] If we first neglect the fluctuations of the localized spins and consider the regime where the moments are aligned by the magnetic field, the Kondo term in the Hamiltonian is replaced with $J\Sigma_i\vec{S}_i\cdot\vec{\sigma}_i=-JS\Sigma_i\sigma^z_i$. The effective magnetic field experienced by the electrons is $H-H^0_e$, where $H^0_e=JS/(g\mu_B)$ is a compensating magnetic field if $J>0$. At $H=H^0_e$, the Hamiltonian is the same as for the compound without the magnetic ions ($J=0$) at zero field. As λ-$(BETS)_2GaCl_4$ is a superconductor, this mapping shows that λ-$(BETS)_2FeCl_4$ has to be a superconductor as long as $|H-H^0_e|<H_P$, the Pauli limiting field. The nature of the superconductivity in the two materials should therefore be the same. This is supported experimentally by similar thermodynamic quantities in both compounds ($T^{Ga}_c=5.5$ K and $T^{Fe}_c=4.2$ K; $H^{Ga}_P=12$ T and $H^{Fe}_{c,max}-H_e\sim 10$ T). Tilting of the magnetic field out of plane giving a perpendicular component of 4 T destroys the superconductivity.[4] This value is comparable to

the upper critical field for λ-$(BETS)_2GaCl_4$ for perpendicular fields.[5] Note also that even if the magnetic field is in the plane, the orbital limiting field must be larger than H_e^0 to get superconductivity. This explanation gives $J=1.6$ meV for $H_e^0=33$ T.[4]

Effects of the fluctuations of the localized spins. The above argument neglects the spin flip terms $J\Sigma_{\mathbf{i}}(S_{\mathbf{i}}^+\sigma_{\mathbf{i}}^- + S_{\mathbf{i}}^-\sigma_{\mathbf{i}}^+)$ in the Hamiltonian, where the $+,-$ superscripts denote spin raising and lowering operators, respectively. Without the fluctuations, the two spin states of the electrons have the same energy for $H=H_e^0$. This is no longer the case when the spins fluctuate: the spin down can flip while the spin $S^z=-S$ is raised to $1-S$ at the same time. Flipping of the spin up is, however, blocked because it would require lowering the spin of the $S_z=-S$ state. These processes renormalize the compensating magnetic field. To gain some insight on the relative importance of this effect, we consider the simple problem of just one local moment and one electron. The compensating magnetic field is then given by (when $g\simeq g_a$) $H_e=[(4S-1)/(4S-2)]H_e^0$ (this reduces to H_e^0 for small fluctuations, i.e., large S). The real value of J is therefore slightly larger than that extracted above. The second effect of the fluctuations is to increase the on-site repulsion between electrons. Two electrons on the same site cost not only the energy U but also block the fluctuations because the spin down is no longer allowed to flip. This extra repulsion is given by $JS/(4S-2)$, which is negligible compared to U. In summary, due to the large value of S, spin fluctuations associated with the local moments do not significantly change the physics.

In order to more clearly establish that the field-induced superconductivity is due to the compensation effect, it is desirable to have an independent measurement of the exchange field. We now show how to extract H_e from the Shubnikov–de Haas oscillations. In layered organic metals a magnetic field perpendicular to the layers will produce oscillations in the resistivity that can be related to Fermi surface parameters.[18] In λ-$(BETS)_2FeCl_4$ at high magnetic field, the magnetic ions impose an exchange field that splits the conduction bands (for spins up and down). We calculate the two corresponding frequencies that should appear in the oscillations. In the absence of an exchange field, as the magnetic field is tilted at an angle θ away from the normal to the layers, the oscillatory part is of the form $\cos[2\pi F/(H\cos\theta)]$ where F is the oscillation frequency. The amplitude of the oscillations is proportional to the spin splitting factor $R_s=\cos(\pi S_0/2\cos\theta)$, where the argument is proportional to the ratio of the Zeeman splitting to the Landau level splitting, $S_0=g^*m^*/m_e$, with renormalized mass and g-factor.[19] In the presence of the exchange field, the spin-splitting factor is modified.[19] We get $R_s=\cos[\pi S_0(H_e/H-1)/2\cos\theta]$. The effect of this is to produce two oscillation frequencies, $F/\cos\theta\pm\delta F$ where $\delta F=S_0H_e/(4\cos\theta)$. In λ-$(BETS)_2FeCl_4$, Uji *et al.* observed two frequencies with a difference of 130 T/$\cos\theta$.[9] If we interpret the frequency difference as due to the exchange field,[20] we extract $H_e=32$ T using the observed effective mass $m^*/m_e=4.1$, and assuming $g^*=g$.[21] Thus the magnetic oscillations imply that the compensating field should be about 32 T, in remarkable agreement with the optimal field for superconductivity.

Electron spin resonance. The frequency splitting discussed above occurs independently of the sign of J. It can be determined unambiguously by electron spin resonance (ESR). In the presence of the exchange field, the ESR frequency in the high-field regime, $\omega=g\mu_B|H-H_e|$,[22] will give H_e and its sign.

Based on the above picture and the analysis below we predict field-induced superconductivity in κ-$(BETS)_2FeBr_4$. It is an AF metal below 2.5 K, and undergoes a superconducting transition at 1 K.[23] The magnetic oscillation spectrum also has two frequencies with a difference of 100 T/$\cos\theta$ and an effective mass of $m^*/m_e=8$.[24] This gives an exchange field of $|H_e|=12$ T. The critical field data for κ-$(BETS)_2GaBr_4$ are not available; but we can estimate H_P from the critical temperature assuming a BCS relation[17] $H_P^{Ga}\sim 1.8k_BT_c/\mu_B=1.2$ T. With the above values for H_e and H_P we would expect field-induced superconductivity in the range 11 to 13 T if $J>0$.

We now show how the upper critical field parallel to the layers can be greatly reduced when there is co-existing superconductivity and AF ordering of the magnetic ions. This has been dramatically demonstrated in λ-$(BETS)_2FeCl_4$ under a pressure of 3.5 kbar. It is an AF metal above 3 kbar (Ref. 25) and undergoes a superconducting transition at about 1 K.[26] Normally, in layered superconductors the upper critical field parallel to the layers is much larger than for the field perpendicular to the layers. Here, the reverse happens! The upper critical field parallel to the layers is only $H_{c2}^{\parallel}=0.05$ T, whereas the perpendicular critical field is about 0.5 T.[26] This is in contrast with the Pauli limiting value estimated from the transition temperature, $H_P=2$ T. We now show that this rapid destruction of superconductivity by a magnetic field is due to the polarization of the magnetic ions and it can be related to the exchange field. In the AF phase, the uniform component of the spins when a magnetic field is applied is $\langle S_z\rangle(H,T)$ leading to an exchange field: $J\langle S_z\rangle(H,T)$. Provided that the crystal structures of the compounds with and without the magnetic ions are similar, the upper critical fields of both compounds are related by $|J\langle S_z\rangle[H_{c2}^{\parallel,\mathrm{Fe}}(T),T]-g\mu_BH_{c2}^{\parallel,\mathrm{Fe}}(T)|=g\mu_BH_P^{Ga}(T)$. Measuring the upper critical fields and the magnetization curve allows a value for J to be extracted. For a classical antiferromagnet with exchange J_0, the transverse magnetization is given by $g_a\mu_BH/(4zJ_0)$ at zero temperature. The relation then becomes $|1-g_a/4zgJ\chi(Q)|H_{c2}^{\parallel,\mathrm{Fe}}=H_P^{\mathrm{Ga}}$. This shows that $H_{c2}^{\parallel,\mathrm{Fe}}$ can be much smaller than H_P^{Ga} [because $J\chi(Q)\sim J/E_F\ll 1$].

We now apply these ideas to κ-$(BETS)_2FeBr_4$. The influence of the magnetic ions has previously been invoked to explain why the upper critical field is anisotropic within the plane of the BETS molecules.[23] We rewrite the relation above between upper critical fields as $|1-H_e/H_N|=H_P^{\mathrm{Ga}}/H_{c2}^{\parallel,\mathrm{Fe}}$, having introduced the classical field to align the moments, $H_N=4zSJ_0/g_a\mu_B$.[27] This allows us to extract the parameter H_e (or J) from the measurements of the critical fields. In κ-$(BETS)_2FeBr_4$, $H_{c2}^{\parallel,\mathrm{Fe}}\sim 1$ T for $H\|c$, H_N

~ 5 T,[23] and $H_P^{\mathrm{Ga}} \sim 1.2$ T (see above). The positive solution is $H_e \sim 10$ T, consistent with the estimate above.

In conclusion, we have stressed the possibility of having a *Mott* insulator in λ-$(BETS)_2FeCl_4$ at zero magnetic field. The measurement of the charge gap as a function of field may help distinguish the Mott versus SDW insulator: for the Mott picture the gap should not vary significantly with field whereas for the SDW picture it should. Furthermore, we have shown that the Hamiltonian that describes λ-$(BETS)_2FeCl_4$ at high fields is simply related to that for λ-$(BETS)_2GaCl_4$ with a compensating magnetic field acting on the spins. We have interpreted the splitting of the magnetic oscillations as a signature of the exchange field, thus allowing us to extract the Kondo coupling. The strength of the exchange field equals that of the optimal field at which superconductivity is observed. This strongly supports the Jaccarino-Peter effect and suggests that the nature of the superconductivity is the same in both materials. Using the same procedure, we have predicted that κ-$(BETS)_2FeBr_4$ should also exhibit a field-induced superconducting phase at about 10 T.

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