Spin Diffusion and Magnetic Eigenoscillations Confined to Single Molecular Layers in the Organic Conductors κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X (X = Cl, Br)

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The layered organic compounds, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X (X = Cl, Br) are metals at ambient temperatures. At low temperatures, the Cl compound is a weakly ferromagnetic Mott insulator while the isostructural Br compound is a superconductor. We find by conduction electron spin resonance and antiferromagnetic resonance (AFMR) an extreme anisotropy of spin transport and magnetic interactions in these materials. In the metallic state spin diffusion is confined to single molecular layers within the spin lifetime of 10^{-9} s. Electrons diffuse several hundreds of nm without interlayer hopping. In the magnetically ordered insulating phase of the Cl compound we observe and calculate the four AFMR modes of the weakly coupled single molecular layers. The interplane exchange field is comparable or less than the typically 1 mT dipolar field and almost 10^6 times less than the intralayer exchange field.

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In quasi two-dimensional conductors the anisotropy may be so high that the $1/\tau_{\parallel}$ intralayer momentum scattering rate exceeds the tunneling rate from one atomic or molecular layer to the next. In such conductors charge transport perpendicular to the layers is incoherent [1]. The condition for conduction electron spin transport to be two dimensional is more stringent: spins in adjacent molecular layers must not mix within the spin lifetime, T_1. In layered organic conductors T_1 is typically 1 ns, several orders of magnitude longer than $\tau_{\parallel}$, and the anisotropy of the momentum scattering has to be extreme for a two-dimensional spin diffusion.

The magnetic resonance experiments described below show that adjacent layers of the isostructural organic compounds, κ-(ET)$_2X$ [κ-(ET)$_2X$ is κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, X = Cl, Br, and ET = BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene], are to a large extent magnetically isolated, testifying two-dimensional spin dynamics. In the metallic state, spin diffusion is confined to single layers. In the ordered state, magnetic eigenoscillations of adjacent layers in external fields are almost completely independent, except in some mode crossing directions. We are not aware of any other layered crystal in which two-dimensional spin diffusion or independent oscillations of adjacent magnetic layers was observed. Previous conduction electron spin resonance (CESR) had insufficient resolution and antiferromagnetic resonance (AFMR) studies in κ-(ET)$_2X$ were inconclusive [2–4].

κ-(ET)$_2$Cl and κ-(ET)$_2$Br have an orthorhombic crystallographic cell [5,6] with two symmetry-related, chemically equivalent ET layers, A and B, separated by polymeric anion layers (Fig. 1). The ET molecules are arranged into dimers with formally $+e$ charge and $1/2$ spin. Interdimer overlap is significantly less than intradimer overlap, and electronic bands are half filled. At high temperatures the conductivity is metallic and very anisotropic: perpendicular conductivity measured by dc methods is about 1000 times less than in-plane [7]. κ-(ET)$_2$Cl undergoes a metal-insulator Mott transition at 27 K and the ground state is a canted antiferromagnetic insulator [8]. A small pressure suppresses the Mott transition in κ-(ET)$_2$Cl, which becomes a superconductor below 12.5 K, similarly to κ-(ET)$_2$Br at ambient pressure [9,10].

We first discuss the CESR in the metallic phase between 45 and 250 K. In magnetic fields, $\boldsymbol{H}$, in general directions there are four differently oriented, magnetically inequivalent ET dimers, $A1$, $A2$ and $B1$, $B2$. Whether lines of molecules are resolved in electron spin resonance (ESR)

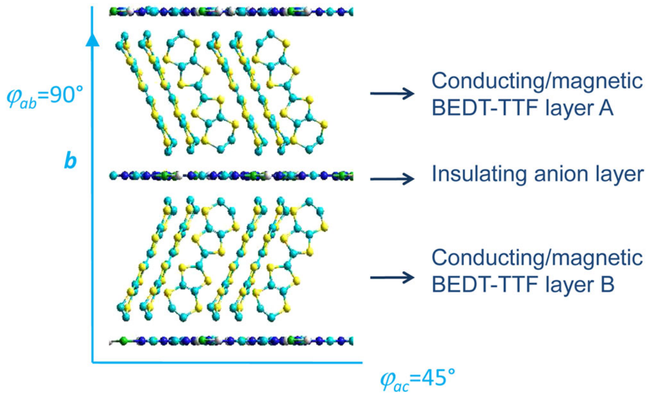

FIG. 1 (color online). Crystal structure of the κ-(ET)$_2X$, X = Cl, Br layered compounds. φ_{ab} and φ_{ac} denote angles from $\boldsymbol{a}$ in the ($\boldsymbol{a}$, $\boldsymbol{b}$) and ($\boldsymbol{a}$, $\boldsymbol{c}$) planes, respectively. Electronic overlap between ET molecules in adjacent A and B layers is small, typically $t_{\perp}$ = 0.1 meV. In the metallic state, the Larmor frequencies of the two chemically equivalent but magnetically inequivalent layers, A and B, are different in general magnetic field orientations.

spectra or not depends on the electronic overlap. The ESR lines of inequivalent *and* isolated magnetic molecules are split by the difference in the Larmor frequencies, $\Delta\omega_{12} = (g_1 - g_2)\mu_B H/\hbar$. The ESR of chemically equivalent but differently oriented molecules splits in magnetic fields in general orientations as spin-orbit and crystal-field interactions render the effective gyromagnetic factors, g_1 and g_2 anisotropic. On the other hand, the CESR lines of interacting molecules merge into a single line if their spins are exchanged in a time of $1/\Delta\omega_{12}$. In quasi one- and two-dimensional conductors this "motional narrowing" into a single line depends on the $\nu_\perp$ hopping rate between inequivalent molecular stacks or layers, A and B. The lines merge into a single line if the difference in Larmor frequencies $\Delta\omega_{AB} < \nu_\perp$ but there are two lines if $\Delta\omega_{AB} > \nu_\perp$. At the relatively low Larmor frequency of 9 GHz, a single CESR line appears in most quasi one-dimensional organic conductors [11] and in the κ-$(\mathrm{ET})_2X$ two-dimensional organic conductors.

Surprisingly, CESR lines of the inequivalent A and B layers in κ-$(\mathrm{ET})_2X$ are clearly resolved in the 222.4 GHz spectra [Fig. 2(a)] at magnetic fields in general directions: two equal intensity lines appear with differently oriented g-factor tensors, g_A and g_B. The assignment of these lines to layers A and B, respectively, is unambiguous. There is a single line at magnetic fields in the $(\boldsymbol{a}, \boldsymbol{c})$ and $(\boldsymbol{b}, \boldsymbol{c})$ planes, where A and B layers are magnetically equivalent, but the line is split in all other directions. A common principal axis of g_A and g_B coincides with the crystallographic $\boldsymbol{c}$ axis while the other two are rotated from $\boldsymbol{a}$ and $\boldsymbol{b}$ by $-30°$ and $+30°$ for g_A and g_B, respectively [Fig. 2(b)]. Overlap between $A1$ and $A2$ dimers within metallic layers is large, typically $t_\parallel = 0.1$ eV, more than sufficient to merge their ESR into a single line. The g-factor anisotropy of a single κ-$(\mathrm{ET})_2\mathrm{Cl}$ layer resembles that of κ-$(\mathrm{ET})_2\mathrm{Cu}_2(\mathrm{CN})_3$ [12], which has a monoclinic crystal structure with one type of layer. Results were reproduced for several samples and were similar for $X = \mathrm{Cl}$ and Br. Twinning was excluded by X-ray diffraction. The splitting is temperature independent and is proportional to the frequency for 111.2 and 222.4 GHz. At 9 GHz the lines might be motionally narrowed, if not then the splitting is obscured by the linewidth determined by the $T_1 = 10^{-9}$ s spin lifetime.

The smallest resolved splitting gives a higher limit of the interlayer hopping rate. At 222.4 GHz the CESR is unambiguously split by 4 mT $= \hbar\Delta\omega_{\min}/g\mu_B$ at $\boldsymbol{H}$ tilted by 10° from the $\boldsymbol{a}$ direction [Fig. 2(b)]. Thus interlayer hopping is extremely rare, and spins are confined to a single molecular layer for $\tau_{\mathrm{spin}} \geq 1/\Delta\omega_{\min} = 1.4$ ns, which is longer than the spin-lattice relaxation time, T_1. This means that in effect spin diffusion is two-dimensional and spins diffuse to a distance $\delta_{\mathrm{spin}\parallel} = \frac{1}{2} v_F (\tau_\parallel \tau_{\mathrm{spin}})^{1/2} \geq 0.2\ \mu$m without mixing with spins in adjacent molecular layers. Here $v_F = 10^5$ m/s is the Fermi velocity [13], and $\tau_\parallel \geq 10^{-14}$ s since the mean free path, $l = v_F \tau_\parallel$, exceeds the average dimer-dimer distance of 10^{-9} m.

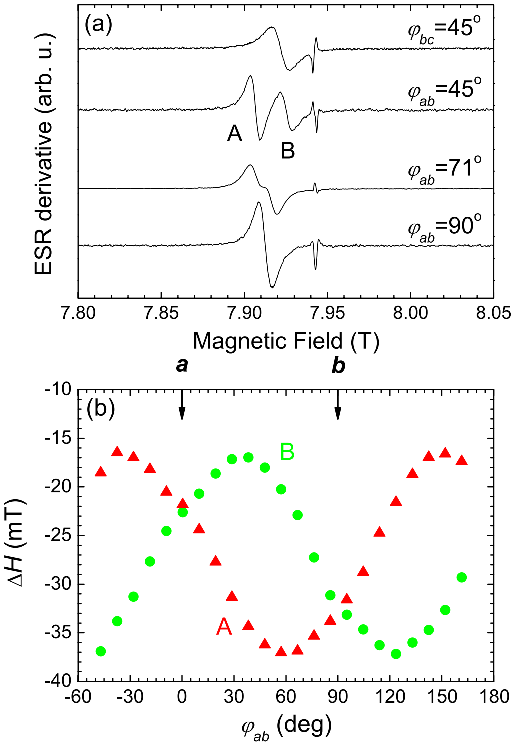

FIG. 2 (color online). Conduction electron spin resonance in κ-$(\mathrm{ET})_2\mathrm{Cl}$ at 222.4 GHz and 250 K. (a) Typical derivative CESR spectra. The resolved lines of A and B layers at fields in general directions ($\varphi_{ab} = 45°$ and $\varphi_{ab} = 71°$) prove the two dimensionality of spin diffusion. When the A and B layers are magnetically equivalent ($\varphi_{ab} = 90°$ and $\varphi_{bc} = 45°$) a single line appears. The KC_{60} reference at $H_0 = 7.94$ T has a g factor of $g_0 = 2.0006$. (b) Angular dependence of the CESR shift $\Delta H = H_0(g_0 - g)/g$ in the $(\boldsymbol{a},\boldsymbol{b})$ plane. The principal axes of the g-factor tensors in the A and B layers are tilted from the orthorhombic $\boldsymbol{a}$ and $\boldsymbol{b}$ axes. It follows from the 4 mT line splitting at $\varphi_{ab} = 10°$ that interlayer spin diffusion is blocked for at least 1.4 ns. Spectra and g-factor anisotropies of Cl and Br compounds are similar.

The transverse charge hopping time is $\nu_\perp^{-1} = \hbar^2/(2t_\perp^2 \tau_\parallel)$ in the incoherent hopping limit [14]; thus, the charge confinement is a consequence of the small interlayer overlap energy, $t_\perp$, and the very short intralayer scattering time, $\tau_\parallel \ll \hbar/t_\perp$. In a simple metallic picture transverse spin and charge hopping times are equal, $\nu_\perp^{-1} = \tau_{\mathrm{spin}}$, and $\tau_{\mathrm{spin}} \geq 1.4$ ns implies $\hbar/t_\perp \geq 5 \times 10^{-12}$ s for κ-$(\mathrm{ET})_2\mathrm{Cl}$. This is the same order of magnitude as $\hbar/t_\perp \geq 16 \times 10^{-12}$ s measured by magnetoresistance at low temperatures in a similar compound, κ-$(\mathrm{ET})_2\mathrm{Cu}(\mathrm{NCS})_2$ [15]. Taking into account the possible contribution of phonons to interlayer hopping would further reduce the estimate of $t_\perp$. We expect that a moderate increase in $t_\perp$ or in $\tau_\parallel$ (e.g., at lower temperature or under pressure) breaks the two-dimensional confinement of spin diffusion. An unexplained line broadening below 50 K prevents testing this in κ-$(\mathrm{ET})_2\mathrm{Br}$. The low interlayer hopping rate suggests a much larger conductivity anisotropy $\sigma_\parallel/\sigma_\perp = (t_\parallel/t_\perp)^2 \times (l/b)^2 = 10^5$–$10^6$ than is measured by dc techniques [7]. Leakage through defects of the insulating polymer may explain this discrepancy [16], although it would result in CESR intensity between the A and B lines, which we do not observe.

In the following, we show that in the magnetically ordered state of κ-(ET)$_2$Cl the magnetic resonance modes of adjacent layers are independently excited in magnetic fields in general directions. Unlike the metallic phase, where perpendicular spin diffusion is not observed, weak interlayer interactions inhibit mode crossing in symmetry planes and are measurable in the magnetically ordered phase.

The low temperature magnetic structure of κ-(ET)$_2$Cl is known in detail from static susceptibility [8] and NMR [17,18]. A magnetic moment of about 0.5 μ_B resides on each dimer. Layers A and B are slightly canted two-sublattice antiferromagnets with large intra- and small interlayer exchange energies, λ and λ_{AB}, respectively. The Dzyaloshinskii-Moriya vectors, $\boldsymbol{D}_\xi$, characterizing the weak ferromagnetism are differently oriented in the $\xi = A$ and B layers: they lie in the $(\boldsymbol{a}, \boldsymbol{b})$ plane at $\varphi_A = 46.5°$ and $\varphi_B = 133.5°$, respectively, from the $\boldsymbol{a}$ axis.

The ESR of κ-(ET)$_2$Cl shifts rapidly with temperature as the antiferromagnetic order develops below the Mott transition at 27 K. In crystals of the highest quality batch the magnetic resonance is narrow at low temperatures [Fig. 3(a)]. The angle dependence of the resonance magnetic field at 4 K was mapped at frequencies 111.2 GHz (Fig. 4) and 222.4 GHz (not shown). The AFMR data of Ohta *et al.* [3] for $\boldsymbol{H} \parallel \boldsymbol{b}$ agree with one of our observed modes. The mode diagrams of the frequency versus resonance field in Fig. 3(b) were calculated numerically at fixed field directions from the free energy, $F = F_A + F_B + F_{AB}$, of weakly interacting adjacent layers and a four-sublattice dynamics:

$$\begin{aligned} F_\xi &= -\boldsymbol{H}\cdot\boldsymbol{M}_\xi - \lambda \boldsymbol{M}_{\xi 1}\cdot\boldsymbol{M}_{\xi 2} + \boldsymbol{D}_\xi\cdot(\boldsymbol{M}_{\xi 1}\times\boldsymbol{M}_{\xi 2}) \\ &\quad + (K_c/2)[(\boldsymbol{M}_{\xi 1}\cdot\hat{\boldsymbol{c}})^2 + (\boldsymbol{M}_{\xi 2}\cdot\hat{\boldsymbol{c}})^2] \\ &\quad + (K_D/2)[(\boldsymbol{M}_{\xi 1}\cdot\hat{\boldsymbol{d}}_\xi)^2 + (\boldsymbol{M}_{\xi 2}\cdot\hat{\boldsymbol{d}}_\xi)^2], \\ F_{AB} &= -\lambda_{AB}(\boldsymbol{M}_{A1}\cdot\boldsymbol{M}_{B1} + \boldsymbol{M}_{A2}\cdot\boldsymbol{M}_{B2}), \end{aligned}$$

where $\boldsymbol{M}_{\xi 1}$, $\boldsymbol{M}_{\xi 2}$ are the sublattice magnetizations of layer ξ with magnitude M_0, $\boldsymbol{M}_\xi = \boldsymbol{M}_{\xi 1} + \boldsymbol{M}_{\xi 2}$, and $\hat{\boldsymbol{c}}$ is the $\boldsymbol{c}$ axis unit vector. We approximated φ_A and φ_B with $\varphi_{A0} = 45°$ and $\varphi_{B0} = 135°$; i.e., we took $\boldsymbol{D}_\xi = D\hat{\boldsymbol{d}}_\xi$ with $\hat{\boldsymbol{d}}_A = [110]/\sqrt{2}$ and $\hat{\boldsymbol{d}}_B = [\bar{1}10]/\sqrt{2}$. K_c and K_D denote single-ion anisotropies with principal axes along $\boldsymbol{c}$ and (for simplicity) $\hat{\boldsymbol{d}}_\xi$, respectively. The computer program calculates the equilibrium directions of $\boldsymbol{M}_{\xi 1}$ and $\boldsymbol{M}_{\xi 2}$ first and then the eigenfrequencies as a function of magnetic field, $\boldsymbol{H}$, oriented in fixed directions. A small damping term towards equilibrium was also added to obtain finite line widths. The g-factor anisotropy and anisotropic terms in the exchange energies were neglected.

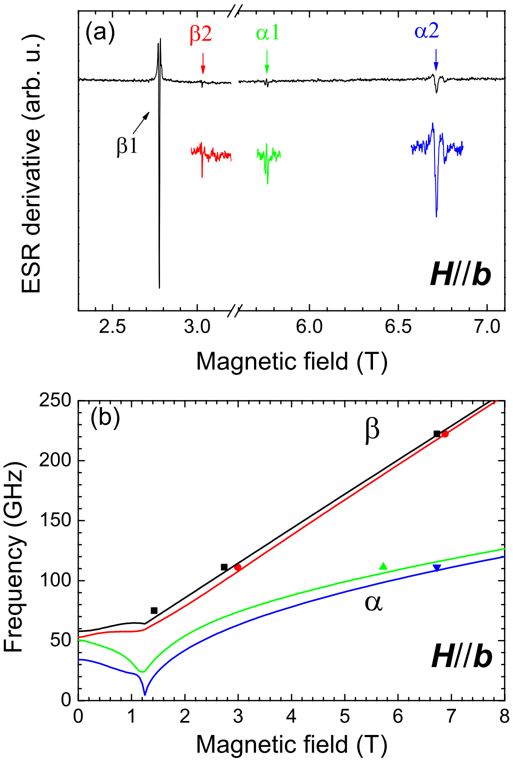

FIG. 3 (color online). Antiferromagnetic resonance in κ-(ET)$_2$Cl at $T = 4$ K and $\boldsymbol{H} \parallel \boldsymbol{b}$. The 4 modes are the α (green, blue) and β (red, black) eigenoscillations of weakly coupled canted antiferromagnetic A and B layers. (a) AFMR spectrum at 111.2 GHz. 5× amplified spectra are shown for higher field lines. (b) Resonance-field-frequency mode diagram. Symbols denote measured AFMR, lines are model calculations.

The eigenmodes for a single layer with $\boldsymbol{H} \parallel \boldsymbol{c}$ are approximately [19]

$$\omega_\alpha/\gamma = \sqrt{DM_0(H + DM_0) + (K_D\lambda M^2)},$$

$$\omega_\beta/\gamma = \sqrt{H(H + DM_0) + (K_c\lambda M^2)},$$

and we denote by α and β the continuation of these modes as the magnetic field angle is varied. The agreement between calculation and experiment is very good at the various frequencies and for all field directions (Figs. 3 and 4). The frequencies depend mainly on DM_0 and the products $\lambda_{AB}\lambda M_0^2$, $K_c\lambda M_0^2$, and $K_c\lambda M_0^2$ but little on the separate values λ_{AB}, K_c, and K_D. With $\lambda M_0 = -450$ T (the average value of Ref. [17]), the best fit parameters are $DM_0 = 3.7$ T, $K_D M_0 = -11$ mT, $K_c M_0 = 2.5$ mT, and $\lambda_{AB} M_0 = 1.15$ mT. The magnitudes of D as determined from AFMR and NMR [18] agree satisfactorily.

The qualitative features predicted for a pair of weakly coupled antiferromagnetic layers are demonstrated by the experiment. At fixed frequencies the α mode resonance field diverges when $\boldsymbol{H}$ is tilted towards $\boldsymbol{D}_\xi$, while the β

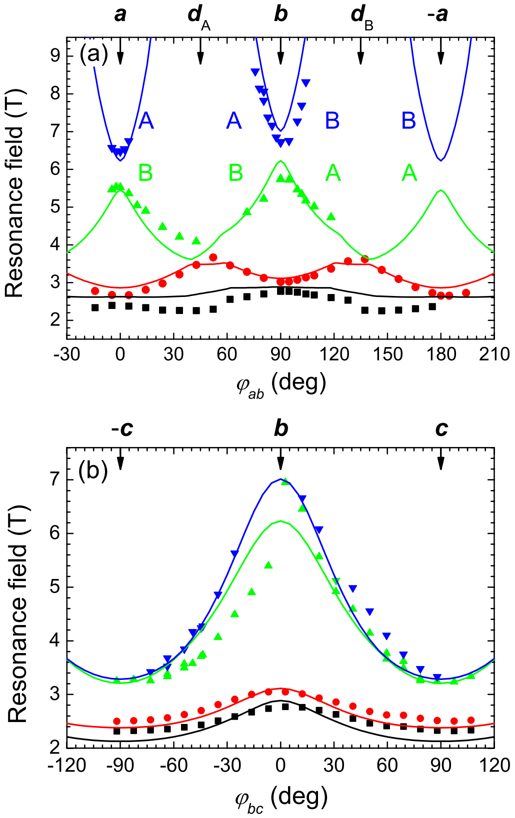

FIG. 4 (color online). Observed (symbols) and calculated (lines) AFMR magnetic fields at 111.4 GHz. (a) In the ($\boldsymbol{a}$, $\boldsymbol{b}$) plane the α modes of A and B layers diverge as $\boldsymbol{H}$ is tilted towards the Dzyaloshinskii-Moriya vectors at $\varphi_{ab} \approx 45°$ and 135°. They are little affected by the interlayer interaction except at mode crossings near $\boldsymbol{a}$ and $\boldsymbol{b}$. (b) The degenerate AFMR mode in the ($\boldsymbol{b}$, $\boldsymbol{c}$) symmetry plane is split by the interlayer interaction. The ±5° uncertainty in sample orientations and approximations in the calculation described in the text explain differences between experiment and theory.

mode has no divergence. Close lying pairs of α and β modes appear in the ($\boldsymbol{a}$, $\boldsymbol{c}$) and ($\boldsymbol{b}$, $\boldsymbol{c}$) symmetry planes. In these planes the interaction between the A and B layers prevents mode crossing; the splitting depends largely on $\lambda_{AB}\lambda M_0^2$, but little on the excitation frequency or angle. The extreme smallness of the interplanar interaction, λ_{AB}, is the most important finding. The magnetic dynamics is two dimensional because λ_{AB} is almost 6 orders of magnitude smaller than the in-plane interdimer exchange interaction λ. We found λ_{AB} ferromagnetic but this may not be meaningful as its magnitude is comparable to the dipolar interaction and we neglected its anisotropy.

In conclusion, at high temperatures spin diffusion in the organic layered conductors is confined to single molecular layers within the spin lifetime. This feature is desirable for materials with spintronic information transfer applications as each molecular layer may serve as an independent channel. Perpendicular transport is strongly incoherent and both superconducting κ-(ET)$_2$Br and antiferromagnetic κ-(ET)$_2$Cl are two-dimensional (and not simply anisotropic) metals at high temperatures. In the ordered magnetic phase the dynamics follows magnetic eigenoscillations of nearly independent single layers; interlayer exchange interactions are comparable or smaller than magnetic dipolar energies. The observed weakly coupled AFMR modes in κ-(ET)$_2$Cl confirms the microscopic model of Smith *et al.* [17,18] and resolves a long standing enigma [3,4]. It remains to be seen how the interlayer coupling changes under pressure.

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