Spin diffusion and magnetic eigenoscillations confined to single molecular layers in the organic conductors \( \kappa-(\text{BEDT-TTF})_2\text{Cu}[\text{N(CN)}_2]X \) \( X=\text{Cl, Br} \)

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The layered organic compounds, \( \kappa-(\text{BEDT-TTF})_2\text{Cu}[\text{N(CN)}_2]X \) \( X=\text{Cl, Br} \) 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 (CESR) 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 hopping to the next molecular layer. 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 inter-plane exchange field is comparable or less than the typically 1 mT dipolar field and almost \( 10^6 \) times less than the intra-layer exchange field.

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In quasi two-dimensional conductors the anisotropy may be so high that the \( 1/\tau_1 \) intra-layer 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 organic layered conductors \( T_1 \) is typically 1 ns, several orders of magnitude longer than \( \tau_1 \), 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, \( \kappa-(\text{ET})_2X \) \( \kappa-(\text{ET})_2X = \kappa-(\text{BEDT-TTF})_2\text{Cu}[\text{N(CN)}_2]X \) \( X=\text{Cl, Br} \), and ET=\text{BEDT-TTF}=bis(ethylenedithio)tetraethiophenylene, 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. The \( 10^6 \) ratio of in-plane to inter-plane exchange fields explains why previous observations \([2, 3]\) were inconclusive. We are not aware of any other layered crystal in which two-dimensional spin diffusion or independent oscillations of adjacent magnetic layers was observed.

\( \kappa-(\text{ET})_2\text{Cl} \) and \( \kappa-(\text{ET})_2\text{Br} \) have an orthorhombic crystallographic cell \([4, 5]\), 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. Inter-dimer overlap is significantly less than intra-dimer 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 \([6]\). \( \kappa-(\text{ET})_2\text{Cl} \) undergoes a metal–insulator Mott transition at 27 K and the ground state is a canted antiferromagnetic insulator \([7]\). A small pressure suppresses the Mott transition in \( \kappa-(\text{ET})_2\text{Cl} \), which becomes a superconductor below 12.5 K, similarly to \( \kappa-(\text{ET})_2\text{Br} \) at ambient pressure \([8, 9]\).

We first discuss the conduction electron spin resonance (CESR) in the metallic phase between 45 and 250 K. In magnetic fields, \( \mathbf{H} \), 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) spectra de-

FIG. 1: (color online) Crystal structure of the \( \kappa-(\text{ET})_2X \), \( X=\text{Cl, Br} \) layered compounds. \( \phi_{ab} \) and \( \phi_{ac} \) denote angles from \( a \) in the \((a, b)\) and \((a, c)\) planes, respectively. Electronic overlap between ET molecules in adjacent A and B layers is small, typically \( 1/t_1 = 0.1 \) 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.
single CESR line appears in most quasi one-dimensional rate, motional averaging into a single ESR line depends on conductors with inequivalent molecular stacks or layers, 1 tors. The ESR lines of interacting molecules merge into a single line. It follows from the 4 mT line splitting that inter-layer spin diffusion is blocked for at least 1 ns spin lifetime, as determined from the CESR line width, gives a similar lower limit for inter-layer hopping. Spins diffuse to a distance \( \delta_s = \frac{1}{2} v_F (\tau_{\text{spin}})^{1/2} \geq 0.2 \mu m \) without hopping to the next molecular layer. Here \( v_F = 10^5 m/s \) is the Fermi velocity, and \( \tau_{\text{spin}} \geq 10^{-14} s \) since the mean free path, \( l = v_F \tau_{\text{spin}} \), exceeds the average dimer–dimer distance of 10\(^{-9}\) m.

The transverse charge hopping time is \( \nu_{\perp}^{-1} = h^2/(2\mu_B^2 \tau_{\perp}) \) in the incoherent hopping limit, thus the charge confinement is a consequence of the small inter-layer overlap energy, \( t_{\perp} \), and the very short intra-layer scattering time, \( \tau_{\perp} \ll h/t_{\perp} \). In a simple metallic picture transverse spin and charge hopping times are equal, and \( \tau_{\text{spin}} \geq 1.4 ns \) implies \( h/t_{\perp} \geq 5 \times 10^{-12} s \) for \( \kappa-(ET)_2Cl \). This is the same order of magnitude as \( h/t_{\perp} \geq 16 \times 10^{-12} s \) measured by magnetoresistance at low temperatures in a similar compound, \( \kappa-(ET)_2Cu(NCS)_{2} \).

We expect that a moderate increase of \( t_{\perp} \) or of \( \tau_{\perp} \) (e.g. at lower temperature or under pressure) breaks the confinement of spin diffusion to a single molecular layer. An unexplained line broadening below 50 K prevents testing this in \( \kappa-(ET)_2Br \). The low inter-layer hopping rate suggests a much larger conductivity anisotropy \( \sigma_{\perp}/\sigma_{\parallel} = (t_{\perp}/t_{\parallel})^2 (l/b)^2 = 10^5 - 10^6 \) than is measured by dc techniques. Leakage through defects of the insulating polymer may explain this discrepancy, 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 or-
the weak ferromagnetism are differently oriented in the β (green, blue) and spectrum at 111 kHz. 

inter-layer interactions inhibit mode crossing in symmetry planes and are measurable 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 inter-layer 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 and NMR. A magnetic moment of about 0.5μ$_B$ resides on each dimer. Layers A and B are slightly canted two-sublattice antiferromagnets with large intra- and small inter-layer exchange energies, λ and λ$_{AB}$, respectively. The Dzyaloshinskii–Moriya vectors, $D_\xi$, characterizing the weak ferromagnetism are differently oriented in the $\xi = A$ and B layers: they lie in the $(a, b)$ plane at $\varphi_A = 46.5^\circ$ and $\varphi_B = 133.5^\circ$, respectively, from the $a$ 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. 3) and 222.4 GHz (not shown). The antiferromagnetic resonance (AFMR) data of Ohta et al. for $H \parallel b$ 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:

$$F_\xi = -H \cdot M_\xi - \lambda M_{\xi1} \cdot M_{\xi2} + D_\xi \cdot (M_{\xi1} \times M_{\xi2}) + (K/2)[(M_{\xi1} \cdot \hat{c})^2 + (M_{\xi2} \cdot \hat{c})^2] + (K_D/2)[(M_{\xi1} \cdot \hat{d})^2 + (M_{\xi2} \cdot \hat{d})^2]$$

$$F_{AB} = -\lambda_{AB}(M_{A1} \cdot M_{B1} + M_{A2} \cdot M_{B2})$$
where \( M_{\xi 1}, \) \( M_{\xi 2} \) are the sublattice magnetizations of layer \( \xi \) with magnitude \( M_0, \) \( M_\xi = M_{\xi 1} + M_{\xi 2}, \) and \( \ell \) is the \( c \) axis unit vector. We approximated \( \varphi_\lambda \) and \( \varphi_\beta \) with \( \varphi_0 = 45^\circ \) and \( \varphi_0 B_0 = 135^\circ, \) i.e., we took \( D_\xi = D d_\xi \) with \( d_\lambda = \frac{1}{\sqrt{2}}[110] \) and \( d_\beta = \frac{1}{\sqrt{2}}[110] \). \( K_\ell \) and \( K_D \) denote single-ion anisotropies with principal axes along \( c \) and (for simplicity) \( d_\ell, \) respectively. The computer program calculates the equilibrium directions of \( M_{\xi 1} \) and \( M_{\xi 2} \) first and then the eigenfrequencies as a function of magnetic field, \( H, \) 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.

The eigenmodes for a single layer with \( H \parallel c \) are approximately [18]:

\[
\omega_\alpha/\gamma = \sqrt{DM_0(H + DM_0) + (K_D\lambda M^2)} \\
\omega_\beta/\gamma = \sqrt{H(H + DM_0) + (K_c\lambda M^2)}
\]

and we denote by \( \alpha \) and \( \beta \) 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 [1]). The frequencies depend mainly on \( DM_0 \) and the products \( \lambda_{AB}\lambda M^2, K_c\lambda M^2, \) and \( K_c\lambda M^2, \) but little on the separate values \( \lambda_{AB}, K_c, \) and \( K_D. \) With \( \lambda M_0 = -450 \) T (the average value of Ref. [16]), 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 magnitude of \( D \) determined from AFMR and NMR [17] agree satisfactorily.

The qualitative features predicted for a pair of weakly coupled antiferromagnetic layers are demonstrated by the experiment. At fixed frequencies the \( \alpha \) mode resonances field diverges when \( H \) is tilted towards \( D_\xi \), while the \( \beta \) mode has no divergence. Close lying pairs of \( \alpha \) and \( \beta \) modes appear in the (\( a, c \)) and (\( b, c \)) symmetry planes. In these planes the interaction between the A and B layers prevents mode crossing; the splitting depends largely on \( \lambda_{AB}\lambda M^2, \) but little on the excitation frequency or angle. The extreme smallness of the inter-planar interaction, \( \lambda_{AB}, \) is the most important finding. The magnetic dynamics is two dimensional because \( \lambda_{AB} \) is almost 6 orders of magnitude smaller than the in-plane inter-dimer exchange interaction \( \lambda. \) We found \( \lambda_{AB} \) 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 \( k-(ET)_2 Br \) and antiferromagnetic \( k-(ET)_2 Cl \) 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; inter-layer exchange interactions are comparable or smaller than magnetic dipolar energies. The observed weakly coupled AFMR modes in \( k-(ET)_2 Cl \) confirms the microscopic model of Smith et al. [16, 17] and resolves a long standing enigma [2, 3]. It remains to be seen how the inter-layer coupling changes under pressure.

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Reference:
[1] For a review, see M. V. Kartsovnik, Chem. Rev. 104, 5737 (2004).
[2] H. Ohta, N. Nakagawa, K. Akioka, Y. Nakashima, S. Okubo, K. Kanoda, and N. Kitamura, Synth. Met. 103, 1914 (1999).
[3] H. Ito, T. Ishiguro, T. Kondo, and G. Saito, Phys. Rev. B 61, 3243 (2000).
[4] A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung, et al., Inorg. Chem. 20, 2555 (1990).
[5] J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, et al., Inorg. Chem. 29, 3272 (1990).
[6] L. I. Buravov, N. D. Kushch, V. A. Merzhanov, M. V. Osherov, A. G. Khomenko, and E. B. Yagubskii, Journal de Physique I 2, 1257 (1992).
[7] U. Welp, S. Fleshler, W. K. Kwok, G. W. Crabtree, K. D. Carlson, H. H. Wang, U. Geiser, J. M. Williams, and V. M. Hitsman, Phys. Rev. Lett. 69, 840 (1992).
[8] H. Ito, T. Ishiguro, M. Kubota, and G. Saito, J. Phys. Soc. Japan 65, 2987 (1996).
[9] S. Lefebvre, P. Wzietek, S. Brown, C. Bourbonnais, D. Jérôme, C. Mézière, M. Fourmigué, and P. Batail, Phys. Rev. Lett. 85, 5420 (2000).
[10] T. Komatsu, N. Matsukawa, T. Inoue, and G. Saito, J. Phys. Soc. Japan 65, 1340 (1996).
[11] A. Kovalev, S. Hill, K. Kawano, M. Tamura, T. Naito, and H. Kobayashi, cond-mat 03, 104 (2003).
[12] N. Kumar and A. M. Jayannavar, Phys. Rev. B 45, 5001 (1992).
[13] J. Singleton, P. A. Goddard, A. Ardavan, N. Harrison, S. J. Blundell, J. A. Schlueter, and A. M. Kini, Phys. Rev. Lett. 88, 037001 (2002).
[14] J. M. McGuire, T. Rööm, A. Pronin, T. Timusk, J. A. Schlueter, M. E. Kelly, and A. M. Kini, Phys. Rev. B 64,
[16] D. F. Smith, C. P. Slichter, J. A. Schluer, A. M. Kini, and R. G. Daugherty, Phys. Rev. Lett. 93, 167002 (2004).

[17] D. F. Smith, S. M. De Soto, C. P. Slichter, J. A. Schluer, A. M. Kini, and R. G. Daugherty, Phys. Rev. B 68, 024512 (2003).

[18] P. Pincus, Phys. Rev. Lett. 5, 13 (1960).