Measurement of interlayer spin diffusion in the organic conductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, X = Cl, Br

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ABSTRACT

In organic conductors the overlap integral between layers is small, in-plane momentum scattering is rapid and transport perpendicular to the layers is expected to be blocked. We present a high frequency conduction electron spin resonance (CESR) study in the layered organic metals κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, X = Cl, Br, which verifies that the inter-layer spin hopping is effectively blocked. The method relies on resolving the CESR lines of adjacent layers in which the orientation of the g-factor tensors differs. We find that at ambient pressure and in the metallic phase the electron spin diffusion is two dimensional in both the X = Cl and Br compounds, i.e. electrons diffuse longer than the spin lifetime within a single molecular layer without inter-layer hopping. Application of pressure at 250 K increases rapidly the inter-layer hopping rate of spins.

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1. Introduction

At ambient temperatures κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X X = Cl, Br (hereafter κ-ET$_2$Cl and κ-ET$_2$Br, respectively), where BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene, are isostructural highly anisotropic, quasi-two-dimensional metals. The conducting BEDT-TTF (or ET) layers [1,2] (Fig. 1) are separated by insulating one-atom-thick anionic polymer sheets. The conduction band is half filled; ET molecules within a layer are arranged into dimers with a charge of $+e$. The overlap energy integral $t_\perp$ between adjacent layers is small, 0.1 meV or less, three orders of magnitude smaller than $t_\parallel$, the typical intra-layer overlap integral between first neighbor ET dimers.

These materials have a rich phase diagram as a function of temperature, pressure and chemical substitution [3]. κ-ET$_2$Cl is an antiferromagnetic Mott insulator below $T_{MI} = 27$ K at ambient pressure. A 30 MPa pressure suppresses the insulating canted antiferromagnetic ground state [4] of κ-ET$_2$Cl and it is a super-

conductor with $T_c = 12$ K. By further increasing the pressure above ~ 0.5 GPa, the ground state becomes metallic. Changing Cl atoms for Br in the anion polymer amounts to applying a "chemical pressure" and the ambient pressure ground state of κ-ET$_2$Br is a superconductor. κ-ET$_2$Br at ambient pressure behaves as κ-ET$_2$Cl under 50 MPa pressure.

The standard description [5] of κ-(ET)$_2$X systems assumes that these are at the borderline of a metal–insulator transition. Small changes in the molecular structure parametrized by the intra-layer overlap integrals change the ground state from insulator to superconductor. The inter-layer coupling plays also an important role, since the ground states are three dimensionally ordered. However, information on the inter-layer coupling is scarce. At low temperatures, $t_\perp$ has been measured in some cases by magnetoresistance, while at higher temperatures the degree of two-dimensionality is usually qualitatively characterized by the conductivity anisotropy. In a previous paper [6] we found that in the metallic phase of κ-ET$_2$Cl the inter-layer hopping is surprisingly slow and that at ambient pressure spin diffusion is two-dimensional. Here we extend CESR measurements at 250 K to high pressures, and the increased inter-layer hopping rate of spins is precisely determined.
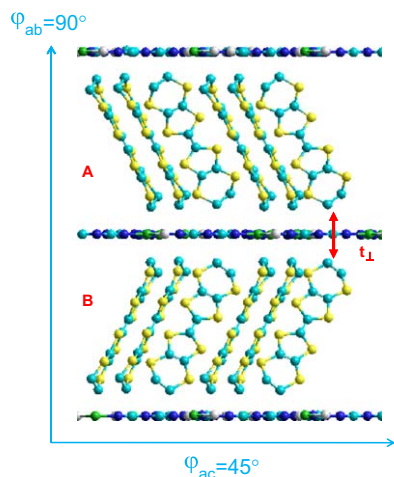
Fig. 1. Crystal structure of the κ-(ET)$_2$Cu[N(CN)$_2$]X X = Cl, Br isostructural layered compounds looking from the **c** direction. A and B denotes two adjacent layers with differently oriented g-factor tensors. φ_{ab} and φ_{ac} denote angles from **a** in the (**a**, **b**) and (**a**, **c**) planes, respectively.

2. Experimental

Single crystals of κ-ET$_2$X X = Cl, Br were grown by the electrochemical method described elsewhere [7]. Twinning of the samples was excluded by X-ray diffraction. A polymeric KC$_{60}$ powder [8] was the g-factor reference (g = 2.0006) for all high-frequency ESR measurements. The g-factor tensors of κ-ET$_2$X X = Cl, Br were determined in Budapest in a home built quasi-optical continuous wave ESR spectrometer at 222.4 GHz with a one-axis goniometer. For the measurements, the sample and the KC$_{60}$ reference were glued with high-vacuum grease close to each other on the rotating axis of the goniometer. The (**a**, **b**) crystallographic plane was aligned with an optical microscope with $\sim 5°$ precision. The pressure dependent ESR measurements were performed in Lausanne at 210 GHz. A copper beryllium clamped-type piston cylinder pressure cell with a diamond window was used [9,10]. In the pressure dependent study the sample was glued by araldite to a teflon holder inside the pressure cell, while the KC$_{60}$ reference was placed to the outer face of the diamond window. The sample was oriented in the $\varphi_{ab} = 45°$ direction with respect to the static magnetic field, as this assures a large difference between the g factors of adjacent layers. φ_{ab} and φ_{ac} denote angles from **a** in the (**a**, **b**) and (**a**, **c**) planes, respectively.

3. Method of measurement of inter-layer hopping rate

The inter-layer hopping rate, $v_\perp$ can be determined from an analysis of the CESR line shape of layered systems with alternating, chemically equivalent but crystallographically different, weakly interacting layers. (See the review Ref. [11] for ESR studies of quasi-one-dimensional organic compounds.) The main parameters of interest for this work are shown in Fig. 2.

The unit cell of the κ-(ET)$_2$X X = Cl, Br crystal has two crystallographically different organic ET layers, A and B (Fig. 1). The conduction electrons within a layer strongly overlap and have common g-factor tensors. Non-interacting adjacent layers have g-factor tensors, g_A and g_B with differently oriented principal axes. In such layers the Larmor frequencies are different in magnetic fields oriented in general directions and there are two CESR resolved lines at frequencies v_A and v_B. Hopping of spins between interacting layers with frequency $v_\perp$ modifies the CESR spectrum.
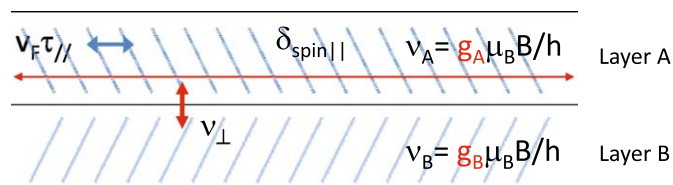

Fig. 2. Relevant parameters for the measurement of inter-layer spin hopping rate, $v_\perp$ between adjacent layers A and B. $g_{A,B}$ are the g factors of the two layers, and **B** is the local magnetic field. Within layers, spins are propagating with the Fermi velocity, v_F and are scattered with frequency $\tau_{\parallel}^{-1} \ll v_\perp$. Spins diffuse to a distance $\delta_{spin\parallel} \gg v_F \tau_{\parallel}$.

Qualitatively, there are three typical cases: (i) if $v_\perp \ll |v_A - v_B|$, there are two resolved lines, slightly broadened and shifted by the interaction, (ii) if $v_\perp \approx |v_A - v_B|$, the line is broad with a characteristic structure, (iii) if $v_\perp \gg |v_A - v_B|$, there is a single "motionally narrowed" line at the average frequency and somewhat broadened by the interaction. For a precise determination of $v_\perp$ we solved the coupled Bloch equations for the transverse dynamic magnetizations, $M_{x,y}^{A,B}$. For layer A:

$$\frac{dM_{x,y}^A}{dt} = \gamma^A (\mathbf{M}^A \times \mathbf{B}^A)_{x,y} - \frac{M_{x,y}^A}{T_2} + \frac{M_{x,y}^B - M_{x,y}^A}{T_\times}. \tag{1}$$

Here $\gamma^A = g_A \mu_B / \hbar$, $\mathbf{B}^A = \mathbf{B}_0 + \lambda \mathbf{M}^B + \mathbf{B}_1$ is the effective magnetic field in the A layer, $\mathbf{B}_1$ the exciting magnetic field, T_2 is the transverse spin relaxation time, $T_\times$ is the cross relaxation between the A and the two adjacent B layers, and $\lambda \mathbf{M}^B$ is the inter-layer exchange field. From these equations, we numerically calculate the CESR spectra. We fit the calculated spectrum to the measured curves and calculate the transverse, cross relaxation times and the exchange field between the layers. The inter-layer spin hopping rate, $v_\perp = (2T_\times)^{-1}$ is half of the cross relaxation rate, as electrons hop from each layer to two adjacent layers. The g-factor anisotropy arises from the spin–orbit interaction with molecules constituting the conducting layer and it is weak in the organic layered ET compounds. Thus for a successful experiment, high exciting frequencies and correspondingly high static magnetic fields, $\mathbf{B}_0$ have to be applied. Also, $v_\perp$ has to be comparable to the CESR line width, which is usually determined in metals by the spin–lattice relaxation rate, $1/T_1$. For the measurement, it is crucial to have two layers in a unit cell with different g-factor anisotropies. Although this restricts the applicability, there are a number of suitable compounds, see e.g. Refs. [12–15] for which the method may work.

4. Results

The g-factor anisotropy of the κ-ET$_2$Cl and κ-ET$_2$Br crystals was measured at 222.4 GHz and T = 250 K in the (**a**, **b**) and (**a**, **c**) planes. In general field directions we observed two CESR lines with equal intensities which merge into a single line in the high symmetry directions **a** and **b** and in the (**a**, **c**) plane. For each orientation we fitted the measured ESR spectrum to a sum of two Lorentzian lines. Close to the high symmetry orientations the analysis gives two nearly overlapping lines and the fit is not better than with the assumption of a single motionally narrowed line. For other directions in the (**a**, **b**) crystallographic plane, two lines are clearly resolved. Results in the (**a**, **b**) plane are presented in Fig. 3. One of the principal axes of the g tensors of the layers coincides with the **c**-axis of the crystal, while the other two are along $\varphi_{ab} \approx 30°$ (-30°) and $\varphi_{ab} \approx 120°$ (60°) in the A (B) layer. We denote these directions by **a**′ and **b**′. κ-ET$_2$Br and κ-ET$_2$Cl have the same g-factor anisotropy within experimental accuracy. The measured principal values of the g-factor tensors for the Cl (Br)

crystals are: $g_{a'} = 2.0062$ (2.0064); $g_{b'} = 2.0088$ (2.0086); $g_c = 2.0050$ (2.0049). The minimum value of $|v_A - v_B|$ at which the CESR lines do not merge sets an upper limit of $v_\perp < 4 \times 10^9$ s^{-1} for the inter-layer hopping frequency of both salts.

A detailed CESR study at various exciting frequencies and at several pressures and temperatures has been preformed and results will be published elsewhere. Here we discuss only the 210 GHz CESR at 250 K measured under 0, 0.16 and 0.32 GPa pressure. These spectra illustrate well the method; at 250 K the perpendicular spin diffusion increases under pressure and a precise determination of $v_\perp$ is possible. Fig. 4 shows the spectra with $\mathbf{B}_0$ in the $\varphi_{ab} = 45°$ direction, where $v_A - v_B$ is about at its maximum. At ambient pressure we clearly see two resolved lines, indicating $v_\perp > v_A - v_B$. Inter-layer hopping broadens the CESR spectrum at 0.16 GPa pressure and $v_A \approx v_B$. Increasing pressure to 0.32 GPa merges the two lines and the spectrum is a motionally narrowed single line; thus $v_\perp < v_A - v_B$. The numerical calculation of the line shapes fit very well the measured CESR spectra. The inter-layer hopping rate, $v_\perp$, at 250 K obtained from the full study, with measurements at 210, 315 and 420 GHz exciting frequencies, are 2.2, 4.2 and 9.7×10^8 s^{-1} at 0, 0.16 and 0.32 GPa pressures, respectively.

5. Discussion

Electron hopping between neighboring layers in quasi-two-dimensional conductors is blocked if the momentum scattering rate $\tau_\parallel^{-1}$ *within* the layers is faster than the tunneling frequency $v_\perp$ *between* layers [16]. The inter-layer hopping frequency for incoherent transport due to weak overlap is [16]

$$v_\perp = 2t_\perp^2 \tau_\parallel / \hbar^2. \quad (2)$$

The rate $v_\perp$ determined from the CESR measurements is in agreement with $t_\perp = 0.04$ meV measured by angular dependent magnetoresistance in κ-ET$_2$Cu(NCS)$_2$ at low temperatures [17] and $\tau_\parallel = 10^{-14}$ s. There are no direct measurements of $\tau_\parallel$ at room temperatures, 10^{-14} s corresponds to a mean free path, $l = v_F \tau_\parallel = 1$ nm, that is equal to the dimer–dimer distance. (Here v_F is the Fermi velocity $\approx 10^5$ m/s.) Since for metallic conductivity, l is longer than the intermolecular distance, 10^{-14} s is an upper limit for $\tau_\parallel$. The CESR measurement of $v_\perp = 2.2 \times 10^8$ s^{-1} and Eq. (2) set a lower limit for the perpendicular transfer integral at 250 K and ambient pressure: $t_\perp < 0.07$ meV. The measured inter-layer hopping frequency includes hopping due to phonons and possibly other mechanisms in addition to incoherent electron tunneling; if such effects are important, then $t_\perp$ is even smaller.

Electron spin transport is thus extremely anisotropic. The average distance spins travel without hopping to an adjacent layer, is $\delta_{spin\parallel} = v_F [\tau_\parallel / (4v_\perp)]^{1/2}$. In the κ-ET$_2$X X = Cl, Br compounds electrons are confined to a single molecular layer for about 2.5×10^{-9} s and $\delta_{spin\parallel}$ is longer than 0.3 μm.

The values of $t_\perp = 0.07$ meV and $t_\parallel = 100$ meV are in disagreement with measured conductivity anisotropies, if perpendicular transport is solely due to tunneling. The tunneling electronic conductivity anisotropy [16] is $\sigma_\parallel / \sigma_\perp \approx 4(t_\parallel / t_\perp)^2 (a/d)^2 \approx 10^6$ where a is a lattice constant in the ($\mathbf{a}$, $\mathbf{c}$) plane and d is the
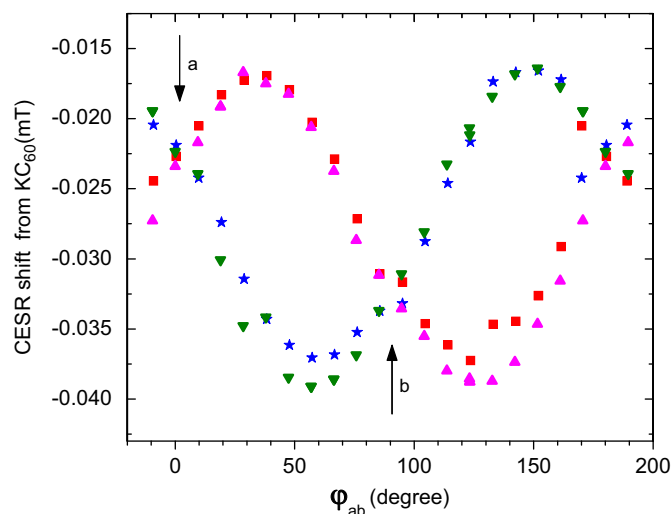

Fig. 3. g-factor anisotropy at 222.4 GHz and $T = 250$ K of the κ-(ET)$_2$Cu[N(CN)$_2$]X X = Cl and Br layered compounds. Up and down triangles (magenta and green, respectively) correspond to the two layers of the κ-ET$_2$Br sample, while stars and squares (blue and red, respectively) belong to the κ-ET$_2$Cl salt. Arrows **a** and **b** represent magnetic field orientations parallel to **a** and **b** crystallographic axes, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
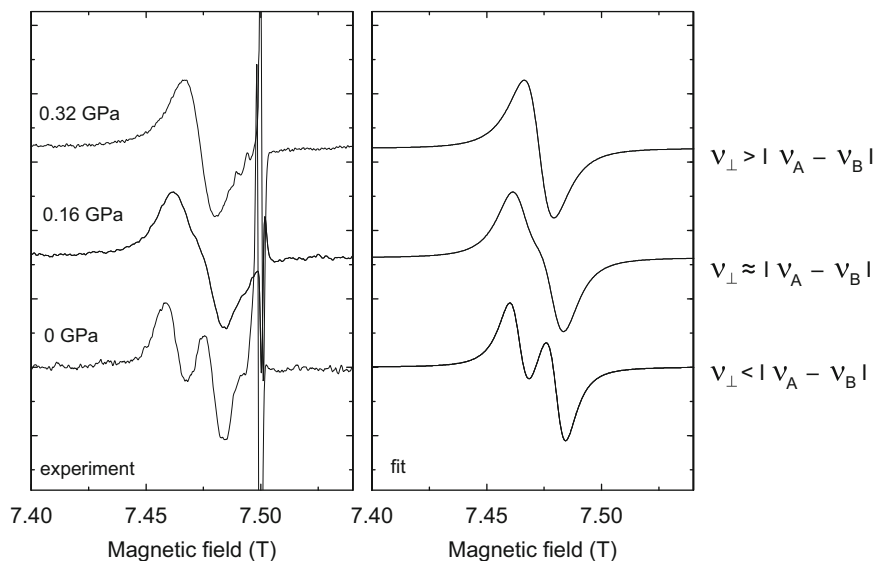

Fig. 4. Motional narrowing of the CESR lines of adjacent layers under pressure. Left panel: measured CESR spectra of κ-(ET)$_2$Cu[N(CN)$_2$]Cl at 210 GHz and $T = 250$ K. The magnetic field is along $\varphi_{ab} = 45°$. The reference signal at B = 7.50 T is polymeric KC$_{60}$. Right panel: simulations of the spectra on the left.

inter-layer spacing. This is much larger than the dc conductivity anisotropy of 10^2-10^3 reported [7,18,19] for κ-ET$_2$X X = Cl, Br compounds.

In conclusion, we measured by high frequency ESR the inter-layer hopping rate with high precision in some strongly anisotropic organic conductors. The study of κ-ET$_2$Br and κ-ET$_2$Cl shows that at 250 K these are very similar, at ambient pressures spin diffusion is quasi-two-dimensional. At 250 K, the inter-layer spin hopping rate increases rapidly with increasing pressure.

Acknowledgements

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