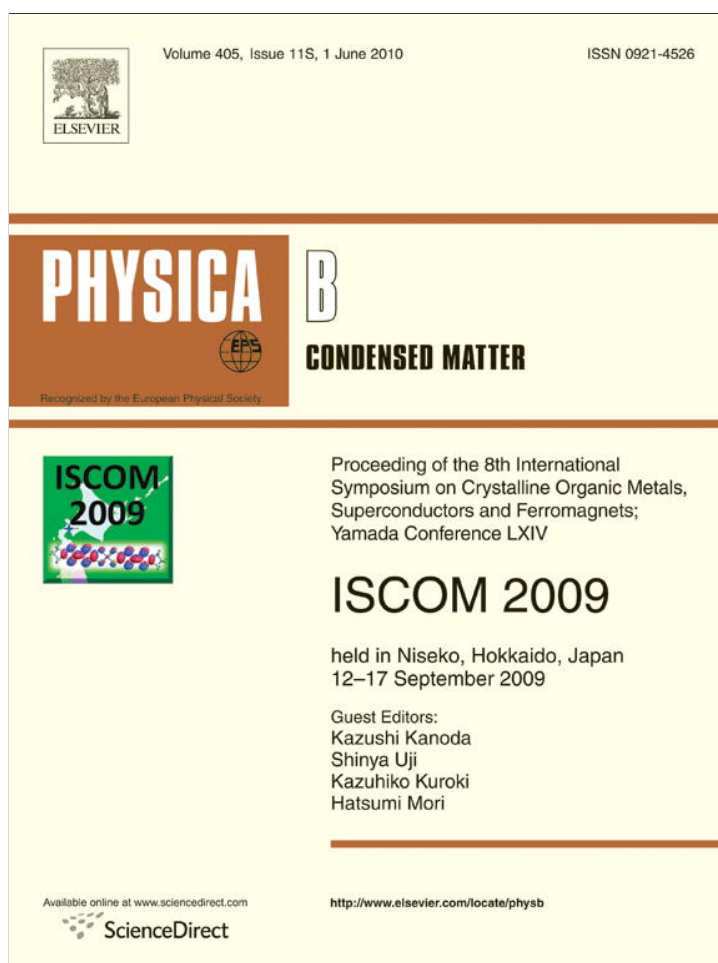




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Magnetotransport properties of a new hybrid metal α -(BEDT-TTF)₂[Mn₂Cl₅(H₂O)₅]

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ABSTRACT

The magnetotransport properties of the α -(BEDT-TTF)₂[Mn₂Cl₅(H₂O)₅] radical cation salt with a new type of magnetic polymeric complex anion, [Mn₂Cl₅(H₂O)₅]_∞[−], are reported. The crystals exhibit metallic behavior down to 0.4 K. Shubnikov-de Haas oscillations, observed at $B > 10$ T, are characterized by two fundamental frequencies, corresponding to cross-sections of the Fermi surface, in agreement with the electronic band structure calculations.

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A lot of interest is currently devoted to hybrid multifunctional materials combining different physical properties. The family of low-dimensional radical cation salts based on organic π -donors with paramagnetic metal complex anions is an important class of such materials (see, for example, Ref. [1]). In recent years a steady progress in the study of organic magnetic conductors has been achieved. Several organic charge-transfer salts with anions containing magnetic ions have been synthesized and characterized. Significant new results have been obtained by using the magnetic anions [MX₄]^{n−} (X=Cl, Br; M=transition metal), [MX(CN)₅]^{3−} (X=CN, NO), [M(C₂O₄)₃]^{3−}, and [M^{III}M^{III}(C₂O₄)₃]^{3−} as well as polyoxometalates.

As a part of our general research effort intending to extend the range of molecular materials combining two properties in the same crystal, we have recently obtained the α -(BEDT-TTF)₂[Mn₂Cl₅(H₂O)₅] radical cation salt. Although there are a number of BEDT-TTF-based conducting charge transfer salts with magnetic chloromanganate anions [2], the title compound is an interesting example because it includes a new type of magnetic polymeric complex [Mn₂Cl₅(H₂O)₅]_∞[−] as counterion and exhibits stable metallic properties down to low temperature. Herein, we report the magnetotransport properties of this new hybrid molecular system.

The structure of α -(BEDT-TTF)₂[Mn₂Cl₅(H₂O)₅] crystals is made of radical cation layers alternating along the a -axis with layers of the polymeric chain anions [Mn₂Cl₅(H₂O)₅]_∞[−] [3]. The asymmetric unit includes two independent donor molecules in general positions, the [Mn₂Cl₅(H₂O)₅] anion in a half-occupied general position and half of the anion unit in a special position on the m -plane. The unit cell contains four donor layers and four anion layers, one donor layer and two anion layers being symmetrically independent.

This α -phase is very different from the classical ones of the α -(ET)₄[MHg(SCN)₄] (M=NH⁴⁺, K⁺, Rb⁺ and Tl⁺) family because the topology of radical cation stacks leads to a set of very isotropic HOMO–HOMO intermolecular interactions. The highly isotropic two-dimensional network of HOMO–HOMO interactions in the present salt is a quite unique situation among α -type salts. It is interesting to note that, albeit being associated with long S...S contacts, the intrastack interactions are quite strong. This is due to the occurrence of four strong S...S contacts, all of them having an almost pure σ -character. These contacts are the result of lateral displacements of the BEDT-TTF molecules, which occur in such a way that the sulfur atoms of the upper molecule are almost straight above the sulfur atoms of the lower molecule. This provides strong interactions within the stacks. The calculated electronic band structure suggests that the salt should be a stable 2-D metal and the conductivity measurements presented below show that it really exhibits metallic behavior in the wide temperature range.

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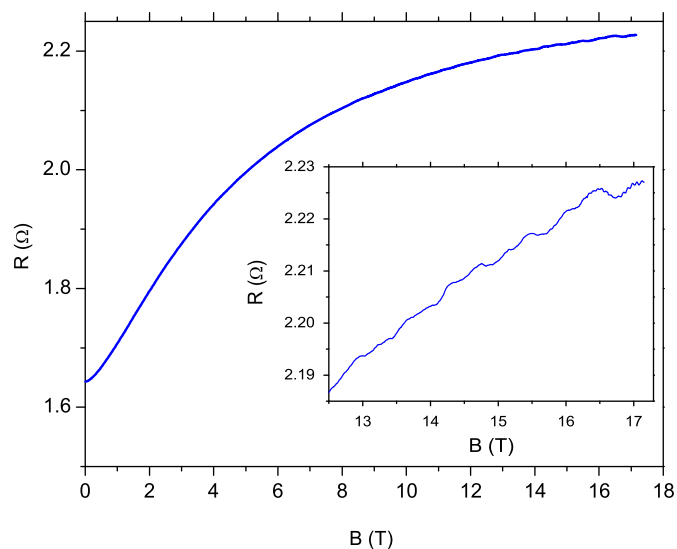


Fig. 1. Magnetic field dependence for the transverse resistance of the α -(BEDT-TTF) $_2$ [Mn $_2$ Cl $_5$ (H $_2$ O) $_5$] single crystal at $T=0.4$ K. The insert makes clear the oscillatory behavior of the resistance at $B > 10$ T.

The sample resistance was measured using a four-probe technique by a lock-in detector at 20 Hz alternating current. Two contacts were prepared to each of two opposite sample surfaces, parallel to (bc)-planes, with conducting carbon paste. The resistance measurements in the temperature range (0.4–300 K) were carried out in a cryostat with a superconducting solenoid, which generated magnetic field of up to 17.2 T.

At room temperature the sample out-of-plane resistivity $\rho_{\perp}$ (300 K) was equal to about 80 Ω cm, which is typical for highly anisotropic quasi two-dimensional organic conductors. The study of $R(T)$ dependences showed that α -(BEDT-TTF) $_2$ [Mn $_2$ Cl $_5$ (H $_2$ O) $_5$] is a molecular metal stable down to 0.4 K. The magnetotransport properties of the single crystals were examined at $T=0.4$ K. The $R(B)$ dependence is presented in Fig. 1 for the field orientation $B||a$. Shubnikov-de Haas (SdH) oscillations, which are quite clear in the expanded scale insert, were found at $B > 10$ T. The oscillation spectrum consists of two main modes with considerably different frequencies. One can see these two oscillation modes separately in Figs. 2 and 3, where the resistance is plotted as a function of the reciprocal of magnetic field. To see the oscillations more clearly, the monotonous component of the $R(1/B)$ dependence is subtracted from the curves for both figures. The high frequency component $F_1=4200$ T is observed in the field interval 16–17.2 T (Fig. 2). The low frequency component $F_2=244$ T, observed in a more wide field region 10–17.2 T, is shown in Fig. 3.

According to energy band calculations, SdH oscillations could result from two kinds of orbits in k-space: the classical orbit α determined by the lens around the Y point of the BZ, and the magnetic breakdown orbit β —ellipse around the point Γ of the BZ. The calculated areas of these orbits lead to the fundamental frequencies of the SdH oscillations $F_{\alpha}=482$ T and $F_{\beta}=4090$ T, respectively. The experimentally observed frequency F_1 is in a fairly good agreement with the value F_{β} (the difference is about 2.5%), while the frequency of the long-period oscillations F_2 is about twice smaller than the value of F_{α} . What may be the possible reason for the difference? Whereas the Fermi surface has been calculated on the basis of the crystal structure at room temperature, the SdH measurements have been carried out at low temperature. The area of the lens decreases when the hybridization of the large ellipses increases, something which occurs when

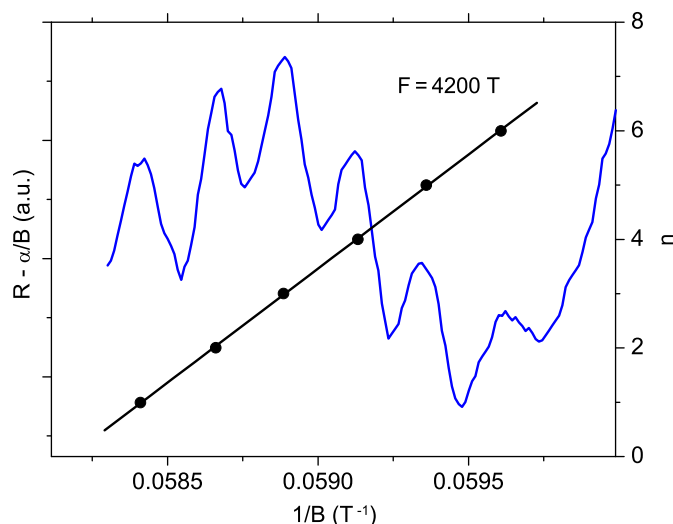


Fig. 2. High frequency component ($F_1=4200$ T) of the Shubnikov-de Haas oscillations at $B > 16$ T. The straight line corresponds to the oscillation maxima positions as a function of the number n and demonstrates the periodicity of the oscillations in $1/B$ scale.

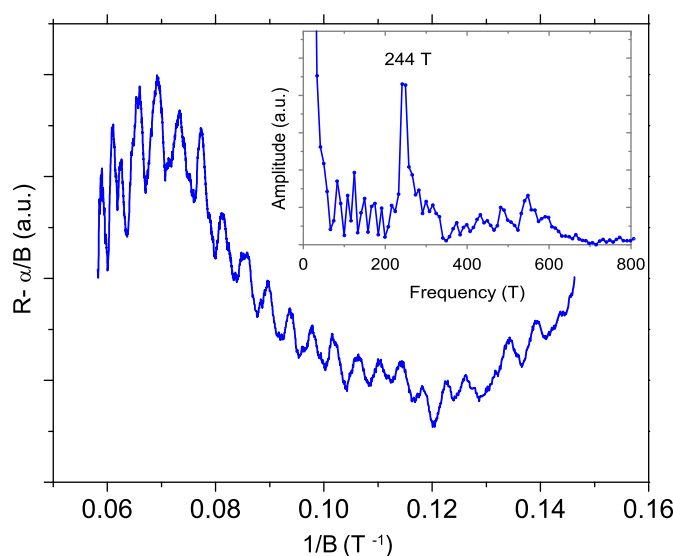


Fig. 3. Low frequency component of the Shubnikov-de Haas oscillations. The Fourier spectrum with the fundamental frequency $F_2=244$ T is shown in the insert.

the stacks are less uniform. Thus we believe that a likely possibility is that the stacks become somewhat less uniform as a result of thermal contraction. Low temperature X-ray work is needed in order to test this suggestion.

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