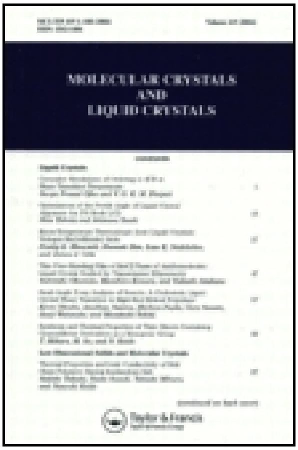

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Anomalous Magnetoresistance in the π-d System $(DIETSe)_2FeCl_4$

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Version of record first published: 31 Jan 2007

To cite this article: Mitsuhiko Maesato, Tomohito Kawashima, Gunzi Saito, Takashi Shirahata, Megumi Kibune & Tatsuro Imakubo (2006): Anomalous Magnetoresistance in the π-d System $(DIETSe)_2FeCl_4$, Molecular Crystals and Liquid Crystals, 455:1, 123-127

To link to this article: http://dx.doi.org/10.1080/15421400600698238

*Mol. Cryst. Liq. Cryst.*, Vol. 455, pp. 123–127, 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600698238

# Anomalous Magnetoresistance in the π-*d* System $(DIETSe)_2FeCl_4$

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*The low temperature transport properties of the π-d system* $(DIETSe)_2MCl_4$ *[M = Fe, Ga] are investigated under the high magnetic fields and high pressures. Anomalous behaviors in the magnetic field dependence of resistance are observed in the magnetic Fe salt below about 2 K, while such anomalous behaviors are absent in the nonmagnetic Ga salt, suggesting the strong interaction between the itinerant π-electrons and the localized moments of d-electrons in* $(DIETSe)_2FeCl_4$.

**Keywords:** π-*d* system; high magnetic field; high pressure; magnetoresistance; organic-inorganic hybrid

## INTRODUCTION

The iodine-substituted donor molecules are promising for the crystal engineering of functional molecular materials using "*iodine bond*" [1]. The charge transfer salts composed of the DIETSe (diiode

This work was partially supported by a COE Research on Elements Science (No. 12CE2005), a Grant-in-Aid for Scientific Research on Priority Areas of Molecular Conductors (No. 15073215), and the Grants-in-Aid for Scientific Research (No. 14740209) from the Ministry of Education, Science, Sports and Culture, Japan and the Grants-in-Aid for Scientific Research (No. 15205019) and (No. 14204033) by JSPS.

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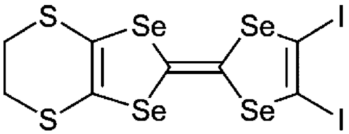


**FIGURE 1** DIETSe molecule.

(ethylenedithio)tetraselenafulvalene) molecule (Fig. 1) and tetrahedral anions $MCl_4^-$ (M = Fe, Ga) have been developed by one of the authors (T. I.) to explore the unique iodine-based donor-anion interaction [2,3]. The magnetic $FeCl_4^-$ anions are successfully introduced in the crystal to produce a new member of magnetic molecular conductors, which are of great interest as the multifunctional molecular materials.

In the present paper, we report the low temperature transport properties of the quasi-one dimensional conductors $(DIETSe)_2MCl_4$ [M = Fe, Ga], which have the three-dimensional donor-anion network based on "*iodine bond*." The purpose of this study is to explore the novel electronic properties due to $\pi$-$d$ interaction.

## EXPERIMENTAL

The electrical resistance of the single crystals was measured using the conventional direct current method. The four gold wires of 15 µm diameter were attached to the crystal with carbon paste as the electrical leads. The typical size of the measured single crystals is $0.6 \times 0.15 \times 0.03\,mm^3$. The small clamp-type nonmagnetic BeCu pressure cell was used for the high-pressure studies. The solenoid-type superconducting magnet was used for the high magnetic field studies.

## RESULTS AND DISCUSSION

The crystal structure of $(DIETSe)_2FeCl_4$ is shown in Figures 2 (a) and (b). The Ga salt is isostructural to the Fe salt. The conducting donor layers and the insulating anion layers are alternately stacked along the $b$ axis. The three-dimensional network of the donor-anion interaction has been observed in the crystal. The donor molecules are uniformly stacked in a column along the $a$-axis direction. The transfer integrals between neighboring molecules are estimated to be $p = -16.6 \times 10^{-2}$, $s = 0.3 \times 10^{-2}$ and $t = -1.5 \times 10^{-2}$ eV from the calculation using the extended Hückel method. The intra-columnar transfer energy is about one order of magnitude larger than the inter-columnar ones, indicating the quasi-one dimensional nature of electronic structure. At ambient pressure, these

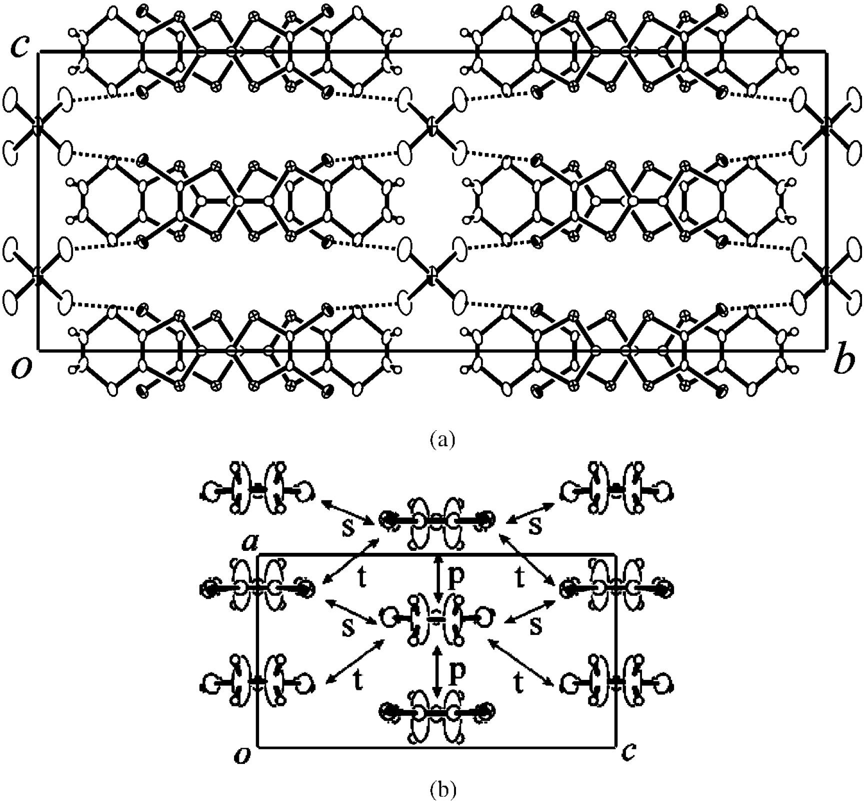
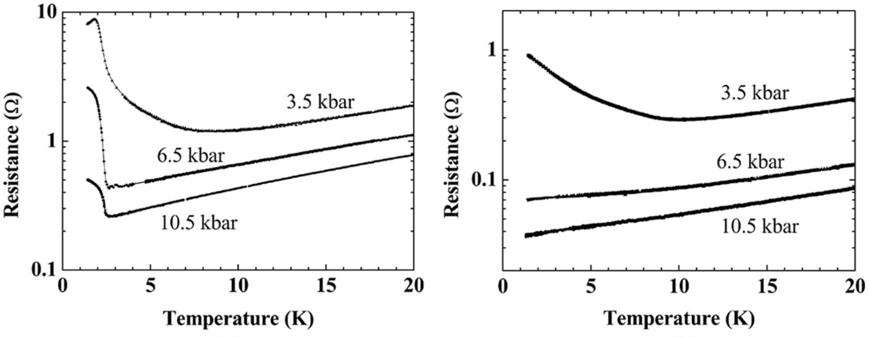


**FIGURE 2** (a) The crystal structure of $(DIETSe)_2FeCl_4$ viewed along the *a* axis. Dotted lines indicate the short I $\cdots$ Cl contacts; (b) The arrangement of donor molecules in the conducting plane and the transfer integrals between them. The transfer integrals are estimated to be $p = -16.6 \times 10^{-2}$, $s = 0.3 \times 10^{-2}$ and $t = -1.5 \times 10^{-2}$ eV.

salts show metallic behavior in the temperature dependence of resistance down to 11–12 K below which semiconducting behaviors are observed [2]. The semiconducting behaviors are possibly due to the nesting instability of the Fermi surface. The semiconducting phase was suppressed by the application of hydrostatic pressure in both salts as shown in Figures 3(a) and (b). It is considered that the warping of Fermi surface is enhanced by the pressure, leading to the suppression of the nesting of Fermi surface.

We also found the additional anomaly in the temperature dependence of resistance at around 2 K in the Fe salt (Fig. 3 (a)), while such anomaly was absent in the Ga salt (Fig. 3 (b)). The anomaly around



(a) (b)

**FIGURE 3** (a) Temperature dependence of resistance of (DIETSe)$_2$FeCl$_4$ under the hydrostatic pressures; (b) Temperature dependence of resistance of (DIETSe)$_2$GaCl$_4$ under the hydrostatic pressures.

2 K persists under the high pressures in the Fe salt. Therefore, the anomaly is not sensitive to the geometrical change of the Fermi surface. The $\mathrm{Fe}^{3+}$ ions have $S = 5/2$ spins, while $\mathrm{Ga}^{3+}$ ions are nonmagnetic. In addition, our preliminary measurement of magnetic susceptibility indicates that the Fe salt shows an antiferromagnetic transition at around 2 K. These results confirm that the anomaly is related to the magnetic order of $\mathrm{Fe}^{3+}$ ($S = 5/2$) spins.

Figure 4 shows the magnetic field dependences of resistance of the Fe salt at 1.5 K under 3.5 kbar. We measured the electrical resistance along the *b* axis. When the magnetic field was applied along the in-plane *c*-axis direction, the magnetoresistance of Fe salt showed a broad peak and a broad dip at around 4 T and 5 T, respectively. When the magnetic field was applied along the inter-plane *b*-axis direction, the magnetoresistance of the Fe salt showed a sharp dip structure at around 1.7 T and a broad maximun at around 2.5 T. Then the magnetoresistance turned to increase above around 5 T. On the other hand, such anomalous magnetoresistance was not observed in the Ga salt. Therefore, the anomalous behaviors of magnetoresistance of the Fe salt below 5 T are probably originated from the changes of magnetic structure of $\mathrm{Fe}^{3+}$ ($S = 5/2$) spins. The present results suggest the strong interaction between the itinerant $\pi$ electrons and the localized moments of *d*-electrons. Further application of pressure enhanced the anomalous behaviors of magnetoresistance in the Fe salt. The details will be reported elsewhere.

In conclusion, the transport properties of the charge transfer salts (DIETSe)$_2$MCl$_4$ [M = Fe, Ga] have been studied to examine the $\pi$-*d*

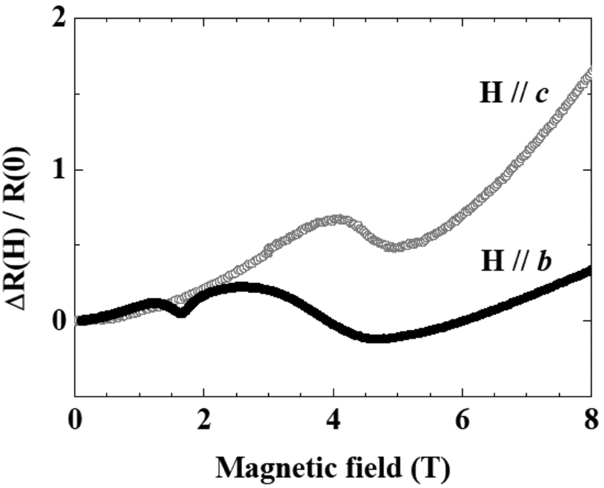


**FIGURE 4** Magnetic field dependence of resistance of $(DIETSe)_2FeCl_4$ at 1.5 K under 3.5 kbar. The magnetoresistance is represented as $\Delta R(H)/R(0) = (R(H) - R(0))/R(0)$. The magnetic field was applied along the *c* axis (open circle) and *b* axis (closed circle).

interaction which might be caused by unique iodine-based donor-anion interaction. At ambient pressure, these are metallic down to 11–12 K below which semiconducting behaviors are observed, possibly due to the nesting instability of the Fermi surface. The semiconducting phase was suppressed by the hydrostatic pressure in both salts. In the Fe salt, we found the additional anomaly in the temperature dependence of resistance at around 2 K, which persists under the high pressures. On the other hand, such anomaly was absent in the Ga salt, implying that the anomaly is related to the magnetic order of $Fe^{3+}$ ($S = 5/2$) spins. In addition, we found the quite anomalous behaviors in the magnetic field dependences of resistance, suggesting the strong interaction between the itinerant π-electrons and the localized moments of *d*-electrons in $(DIETSe)_2FeCl_4$.

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