

New aspects of π -d interactions in magnetic molecular conductors

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Abstract. The 2 : 1 cation radical salts of bent donor molecules of ethylenedithio-tetrathiafulvalenoquinone-1,3-dithiolemethide (EDT-TTFVO), ethylenedithio-diselenadithiafulvalenoquinone-1,3-dithiolemethide (EDT-DSDTFVO), ethylenedithio-diselenadithiafulvalenoquinone-1,3-diselenolemethide (EDT-DSDTFVSDS), ethylenedioxy-tetrathiafulvalenoquinone-1,3-dithiolemethide (EDO-TTFVO) and ethylenedioxy-tetrathiafulvalenoquinone-1,3-diselenolemethide (EDO-TTFVODS) with FeX_4^- ($X = \text{Cl}, \text{Br}$) ions are prepared by electrocrystallization. The crystal structures of these salts are composed of alternately stacked donor molecule and magnetic anion layers. The band structures of the donor molecule layers are calculated using the overlap integrals between neighboring donor molecules and are compared with the observed electronic transport properties. The magnetic ordering of the Fe(III) d spins of FeX_4^- ions is determined from magnetization and heat capacity measurements. The magnetic ordering temperatures are estimated by considering a combination of a direct d-d interaction between the d spins and an indirect π -d interaction between the conduction π electron and the d spins, whose magnitudes are separately calculated from the crystal structures with an extended Hückel molecular orbital method. The occurrence of a π -d interaction is proved by the negative magnetoresistance, and the magnitude of magnetoresistance reflects the strength of the π -d interaction. The effect of pressure on the magnetoresistance is studied, and the result indicates that the magnitude of magnetoresistance increases, namely, the π -d interaction is enhanced with increasing pressure. From these experimental results it is shown that $(\text{EDT-TTFVO})_2 \cdot \text{FeBr}_4$ is a ferromagnetic semiconductor, $(\text{EDT-DSDTFVO})_2 \cdot \text{FeX}_4$ ($X = \text{Cl}, \text{Br}$) and $(\text{EDT-DSDTFVSDS})_2 \cdot \text{FeBr}_4$ are metals exhibiting antiferromagnetic ordering of the d spins, and $(\text{EDO-TTFVO})_2 \cdot \text{FeCl}_4$ and $(\text{EDO-TTFVODS})_2 \cdot \text{FeBr}_4 \cdot (\text{DCE})_{0.5}$ (DCE = dichloroethane) are genuine antiferromagnetic metals. Among them, the $(\text{EDT-TTFVO})_2 \cdot \text{FeBr}_4$ salt is the first π -d molecular system where the d spins of FeBr_4^- ions are ferromagnetically ordered through antiferromagnetic interaction with the conduction π electrons. Corresponding to this ferromagnetic ordering, an anomalous dielectric slow-down phenomenon toward the ordering temperature is observed. The π -d interaction in $(\text{EDT-DSDTFVSDS})_2 \cdot \text{FeBr}_4$ is very large and comparable to that in λ -(BETS) $_2 \cdot \text{FeCl}_4$, which has the highest reported value so far, while the d-d interaction is fairly small. Concerning the ratio between the magnitudes of π -d and d-d interactions ($J_{\pi d}/J_{dd}$), this salt is currently the best π -d molecular system.

Keywords: bent donor molecule, magnetic FeX_4^- ion, cation radical salt, magnetic molecular conductor, crystal structure, band structure, metallic conductivity, ferro-/antiferro-magnetic ordering,

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