IV-Q Systematic Study of Organic Conductors

Thanks to the systematic view to structure-property relationship studied particularly in BEDT-TTF-based conductors, recently our understanding of organic conductors has made a great progress. From the concept of "universal phase diagram" in the θ-phase, we can predict metal-insulator transition temperatures of a large number of organic conductors. The underlying logic behind this universal view has been explained by the change of orbital overlap between adjacent molecules. Systematization of detailed stacking patterns in the β- and β"- phases has attempted, from which we can make a fairly good prediction to superconducting phases. These universal views are applied to individual cases, in particular to β-(BEDT-TTF)$_2$PF$_6$ family salts with twisted overlap mode, and to α"-phase salts, which are regarded as hybrid of the θ- and β"-phases, and actually whose properties are a complicated mixture of these parent phases.

IV-Q-1 Structural Genealogy of BEDT-TTF-Based Organic Conductors I. Parallel Molecules: β and β" Phases

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A method is proposed to systematize a number of structural modifications of BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene)-based organic conductors and related materials. Analysis of actual crystal structures indicates that most crystal structures are constructed of two essential building blocks: ring-over-bond (RB) and "ring-over-atom" (RA) overlap modes. Several different ways to pile up these elements lead to various structures which are conventionally designated as β, β', β", θ, α, and α"-phases (Figure 1). In the β- and β"-phases, introduction of "dislocations" along the stacking axis generates a number of modifications, where dislocations are interactions of two donor molecules which have larger displacements along the molecular long axis than the standard RB and RA modes. Systematic nomenclature to distinguish these modifications are proposed. Transfer integrals are, however, not very sensitive to the existence of dislocations, so that the Fermi surfaces of these multiple phases are derived from the fundamental structure by folding the first Brillouin zone.

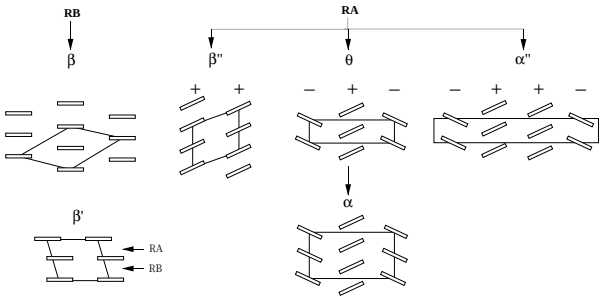

Figure 1. Genealogy of β, β', β", θ, α, and α"-phases; the packing patterns of the donor sheets are viewed along the molecular long axis.

IV-Q-2 Structural Genealogy of BEDT-TTF-Based Organic Conductors II. Inclined Molecules: θ, α, and κ Phases

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Overlap integrals between HOMO's of two non-parallel BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) molecules have been calculated. As the dihedral angle between the molecular planes decreases from 180° (parallel) to 90° (perpendicular), the overlap integral increases and attains a maximum around 90°. This accounts for the "universal phase diagram" of the θ-phase; θ-salts vary from an insulator to a metal with decreasing the dihedral angle (Figure 1). The ratio of the lattice constants in the conducting plane, *c*/*a*, changes in proportion to the dihedral angle. Thus *c*/*a* can be used instead of the dihedral angle. A similar universal phase diagram is applicable to analogous phases like α and α", and also to the corresponding phases of other donors. The properties of κ-phase salts are similarly scaled by *c*/*a*. As *c*/*a* increases, the intradimer overlap integral decreases owing to the increase of the intradimer spacing, and correlated insulator, superconductor, and simple-metal phases appear in succession. When *c*/*a* increases further, another insulating phase emerges due to the decrease of the interdimer overlaps. Chemical pressure in both θ- and κ-phases reduces *c*/*a*, and stabilizes the insulating state. Hydrostatic physical pressure gives the same influence in the θ-phase, but enhances the interdimer interaction in the κ-phase to result in the opposite effect. A diagram is proposed to illustrate which structures of β, β", θ, and κ are favored by BEDT-TTF and other donors.

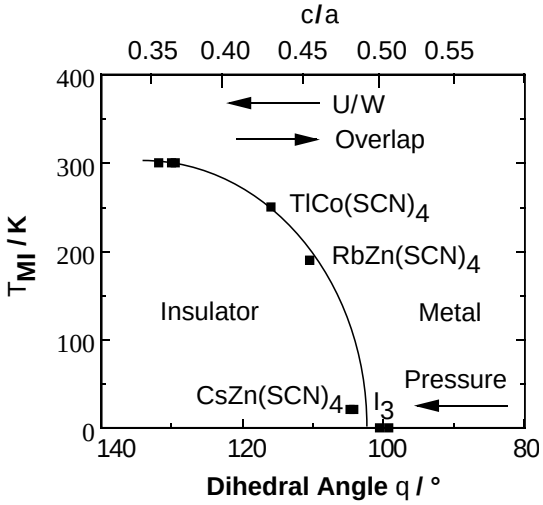

Figure 1. Universal phase diagram of the θ-phase.

IV-Q-3 $2k_F$ CDW Transition in β-(BEDT-TTF)$_2$-PF$_6$ Family Salts

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In an attempt to clarify the nature of the metal insulator transition of β-(BEDT-TTF)$_2$PF$_6$ family salts, temperature dependence of the static magnetic susceptibility, resistivity under various pressures, lattice parameters and the intensity of X-ray superlattice reflections have been measured for β-(BEDT-TTF)$_2$PF$_6$ and β-(BEDT-TTF)$_2$AsF$_6$. The transition temperature (T_{MI}) of these salts is shifted to higher temperatures with an increase of pressure. A sharp drop of the activation energy is observed at 5 kbar for the PF$_6$ salt and 6 kbar for the AsF$_6$ salt (Figure 1). Above these pressures, resistivity becomes almost flat down to low temperatures though the resistivity again increases below 50 K. Phase diagrams were constructed for both materials. Static magnetic susceptibilities of both salts exhibit abrupt drops below T_{MI}. A noticeable drop of the lattice parameters, lattice volumes and the X-ray intensities around T_{MI} indicate that the M-I transition is associated with the structural transition. The existence of the 2-fold structural changes is established by observing the superlattice reflections corresponding to (a, b, $2c$) below T_{MI}.

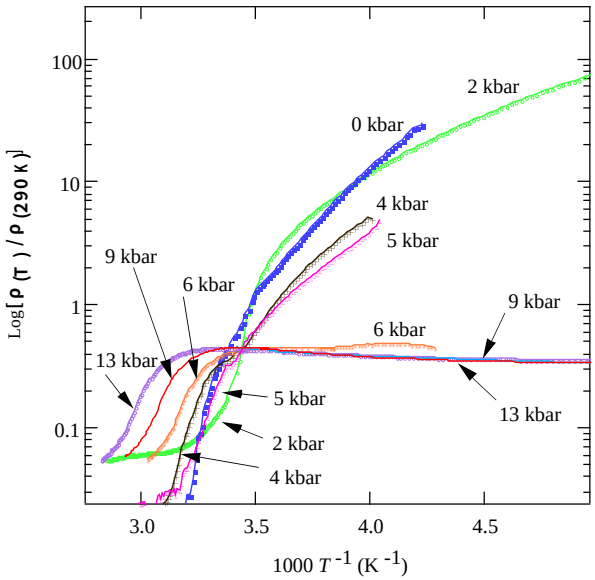

Figure 1. Temperature dependence of normalized resisitivity for the PF$_6$ salt at different pressures: Arrhenius plots.

IV-Q-4 Transport Properties of α”-Phase Organic Conductors, (BEDT-TTF)$_2$CsHg(SCN)$_4$ and (BEDT-TTF)$_2$K$_{1.4}$Co(SCN)$_4$

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[*Physica C* **316**, 243 (1999)]

Under pressure, the metal-insulator transition temperature T_{MI} (210 K) of α"-(BEDT-TTF)$_2$CsHg(SCN)$_4$ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) decreases up to 7 kbar, whereas above this pressure the system becomes more insulating as the pressure increases (Figure 1). This behavior is interpreted in view of the mixed β”-like and θ-like characters of the α”-phase. In this compound two-fold lattice modulation appears much above T_{MI}, even at room temperature. This indicates that the lattice modulation is not the direct origin of the M-I transition. In α”-(BEDT-TTF)$_2$-K$_{1.4}$Co(SCN)$_4$, T_{MI} (130 K) rises very slowly under pressure.

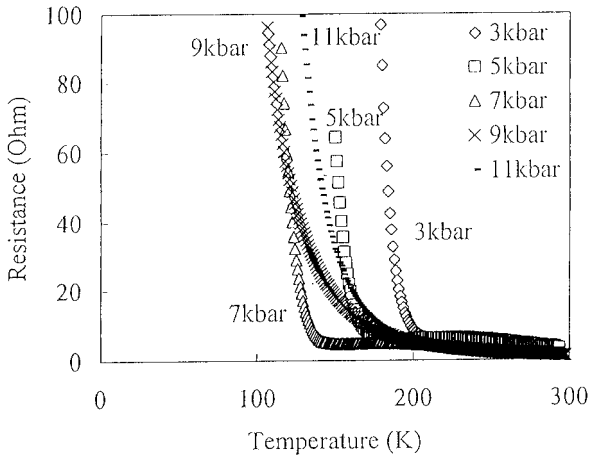

Figure 1. Temperature dependence of electrical resistance of α”-(BEDT-TTF)$_2$CsHg(SCN)$_4$ under applied pressures.