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Modified Chesnut Model for Spin-Crossover Semiconductors $[Fe(acpa)_2](TCNQ)_n$

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Embedding of bistable molecules into an organic conductor is expected to yield interesting hysteretic conductive properties. As a typical bistable species switchable under a temperature change, a spin-crossover iron(III) complex was utilized to prepare two charge-transfer salts containing an organic acceptor molecule, $[Fe(acpa)_2](TCNQ)_n$ (Hacpa = *N*-(1-acetyl-2-propylidene)-2-pyridyl-methylamine; TCNQ = 2,2'-(2,5-cyclohexadien-1,4-diylidene)-bispropanedinitrile), and their magnetic and electrical properties were studied. While magnetic behavior of dilute spin-crossover complex molecules is well described by an entropy-driven spin equilibrium between low-spin and high-spin states across an energy gap, intermolecular interactions should be taken into account and often abrupt phase transitions are found in densely-packed complex molecules like crystalline solids. In order to delineate these systems in a unified manner, a phenomenological two-state model based on a mean-field approximation was examined. It worked well to reproduce the temperature dependence of electrical conductivities associating with a spin-crossover transition assuming a Slater-type distance dependence for the band gap.

Keywords: spin-crossover phenomena; iron(III) complex; TCNQ; Chesnut model; first-order phase transition; band gap

INTRODUCTION

Spin-crossover complexes keep attracting a lot of interest since their molecular bistability is controllable not only thermally but also optically and through other external parameters[1]. For example, some iron(III) complexes show remarkable spin-crossover phenomena from the low-spin ground state (s = 1/2) to the high-spin excited state (s = 5/2) with increasing temperature. If these complexes are embedded into organic conductors, interesting magnetoconductive properties are expected. In order to study how the spin transitions affect electrical conductivities of compounds, we prepared spin-crossover complexes which contain $TCNQ^{\bullet-}$ moieties[2]: $[Fe(acpa)_2](TCNQ)_n$ (Hacpa = *N*-(1-acetyl-2-propylidene)-2-pyridyl-methylamine; TCNQ = 2,2'-(2,5-cyclohexadien-1,4-diylidene)-bispropanedinitrile; n = 1 or 2). The spin-crossover transition of $[Fe(acpa)_2](TCNQ)$ occurs abruptly at 159.5 K, while $[Fe(acpa)_2](TCNQ)_2$ shows rather sluggish transition at around 370 K. Since the latter compound exhibited a relatively high electrical conductivity of $\sigma_{rt} = 2.8 \times 10^{-3}$ S cm^{-1} at room temperature, the detailed temperature dependence was examined.

MODIFIED CHESNUT MODEL

The Chesnut model is one of the simplest phenomenological models applicable to a wide range of cooperative systems, from a strong-interaction limit with first- or second-order phase transitions to negligible-interaction cases behaving as a quasi-equilibrium system, in a unified manner. It has been originally introduced to describe molecular systems exhibiting low-lying triplet states with singlet ground states[3]. Without any intermolecular interactions, such two-level systems are characterized by the free energy for isolated molecules:

$$F_0 = (\Delta H_0 - T\Delta S_0) \bullet \rho + RT[\rho \ln\rho + (1-\rho)\ln(1-\rho)],$$

where ΔH_0 and ΔS_0 stand for the enthalpy and entropy change accompanying with the excitation across the two states, respectively, ρ the fraction of excited molecules, R the gas constant, and T the temperature. Minimizing this free energy ($\partial F_0/\partial\rho = 0$), the expectation value of ρ in non-cooperative systems is easily derived as

$$\rho(T) = 1/\left(1 + \exp\left[(\Delta H_0 - T\Delta S_0)/RT\right]\right).$$

Under a mean-field approximation, the cooperativity of the system is incorporated through an additional interaction term to F_0:

$$F = F_0 + \frac{1}{2} z \bullet \left[\varepsilon_{ee}\rho^2 + \varepsilon_{gg}(1-\rho)^2 + 2\varepsilon_{ge}\rho(1-\rho)\right],$$

where z is the number of neighboring molecules, ε_{ee} the interaction between a couple of excited species, ε_{gg} the interaction between molecules in the ground state, and ε_{ge} the interaction between ground and excited species.

The Chesnut model in its original form assumes only attractive interactions between neighboring excited species, *i.e.* $\varepsilon_{ee} < 0$ and $\varepsilon_{gg} = \varepsilon_{ge} = 0$. This assumption successfully accounts for the first-order phase transitions in some singlet-triplet systems, however, brings about a shortcoming called "overshoot" phenomenon for a certain choice of parameters. When $z\varepsilon_{ee} << -\Delta H_0$, the system undergoes a first-order phase transition with too much gain (overshoot) of ρ at the transition temperature on heating, which decays at higher temperatures. This phenomenon is understood by a symmetry consideration that the above choice of parameters lets ρ be the order parameter of the system so that the high-temperature phase is more ordered (lower symmetry) which should decay owing to entropy effect at higher temperatures[4].

To remove the overshoot phenomena, it is physically reasonable to adopt an order parameter which becomes zero in the high-temperature limit. Thus, it should relieve the ill behavior to take the fraction of ground species, $1-\rho$, as the order parameter, *i.e.* $\varepsilon_{gg} < 0$ and $\varepsilon_{ee} = \varepsilon_{ge} = 0$. This parameter setting never arises the overshoot and is preferable to be applied to spin-crossover systems. Rewriting $-z\varepsilon_{gg} = J$, the free energy

$$F = F_0 - \frac{1}{2} J(1-\rho)^2 \qquad (J > 0),$$

is obtained. This modified Chesnut model is distinguished from original one by the attractive interactions working between the low-spin species instead of the attractive force between the high-spin species.

TABLE 1 Thermodynamic quantities associated with spin-crossover.

$\Delta S_0 / R$	$\Delta H_0 / R$ K	J / R K	$\Delta\rho$	$\Delta H / R$ K	$\Delta S / R$	T_c^* / K
10.0	0.0	1500.0	0.999	750	9.99	75
10.0	1000.0	1500.0	0.970	1698	9.70	175
10.0	2000.0	1500.0	0.798	2198	7.99	275
10.0	2500.0	1500.0	0.606	1965	6.05	325
10.0	2700.0	1500.0	0.491	1702	4.93	345
10.0	3000.0	1500.0	0.134	502	1.34	375
10.0	3200.0	1500.0	0.0	0	0.0	(395)
10.0	2000.0	0.0	0.0	0	0.0	(200)
10.0	2000.0	500.0	0.0	0	0.0	(225)
10.0	2000.0	1000.0	0.152	381	1.53	250
10.0	2000.0	1200.0	0.610	1592	6.12	260
10.0	2000.0	1500.0	0.798	2198	7.99	275
10.0	2000.0	2000.0	0.909	2727	9.09	300
10.0	2000.0	3000.0	0.969	3393	9.70	350
$[Fe(acpa)_2]PF_6$ solution[5]				(2285)	(9.48)	(241)
$[Fe(acpa)_2](TCNQ)$				150		160
$[Fe(acpa)_2](TCNQ)_2$				360		370

* Numbers in parentheses stand for $T_{1/2}$, where $\rho = 0.5$, instead of T_c.

Solving the modified Chesnut model, quasi-equilibrium behavior,

$$\rho(T) = 1/\left(1 + \exp\left[\{\Delta H_0 + J(1-\rho(T)) - T\Delta S_0\}/RT\right]\right),$$

is obtained as a self-consistent equation for the systems with weak cooperativity. Stronger interactions ($J > 4\ RT$) induce a phase transition. When a phase transition occurs at critical temperature T_c accompanying with a discontinuity of the order parameter from ρ_1 to ρ_2, these quantities should satisfy following relations:

$$\Delta\rho \equiv \rho_2 - \rho_1 = \tanh(J \bullet \Delta\rho / 4RT_c),$$

$$T_c = \Delta H / \Delta S, \qquad \Delta H \equiv (\Delta H_0 + \tfrac{1}{2}J) \bullet \Delta\rho, \quad \Delta S \equiv \Delta S_0 \bullet \Delta\rho,$$

where ΔH and ΔS are enthalpy and entropy jumps at T_c, respectively. These equations fully determine the thermodynamic quantities of spin-crossover phase transitions (see Table 1 and Figure 1).

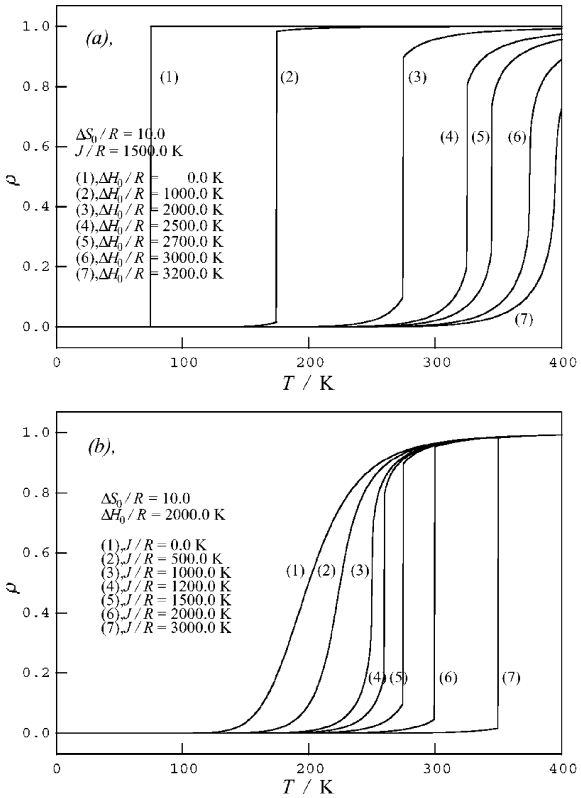

FIGURE 1 Temperature dependence of high-spin fraction ρ of modified Chesnut model for several interaction parameter sets.

TEMPERATURE-DEPENDENT BAND GAP IN $[Fe(acpa)_2](TCNQ)_2$

Since high-spin species has a larger molecular volume than low-spin species, transfer integrals $t(r)$ between neighboring TCNQ moieties should get modulated by the high-spin fraction $\rho(T)$. For simplicity are assumed the linear dilation of TCNQ separations, $r = r_{LS} + (r_{HS} - r_{LS})\rho(T)$, and the Slater-type distance dependence for the transfer integrals between TCNQ LUMO's, $t(r) = t_0 \bullet \exp[-\zeta \bullet r]$. Then the band gap E_g is approximated by the HOMO-LUMO gap E_0 of isolated TCNQ moieties subtracted by the band widths of valence and conduction bands

within a tight-binding model, so that

$$E_g = E_0 - 2\,t(r) = E_0 - 2\,t_0 \bullet \exp[-\zeta \bullet \{r_{LS} + (r_{HS} - r_{LS})\rho(T)\}].$$

Referring the expression of the temperature dependence of electrical conductivity, $\sigma(T) = \sigma_\infty \exp[-E_g/2k_BT]$, conductive behavior of a semiconductor affected by spin-crossover phenomena was worked out. Although the model is rather crude, it qualitatively reproduced the temperature dependence accompanying the first-order phase transition shown in Figure 2.

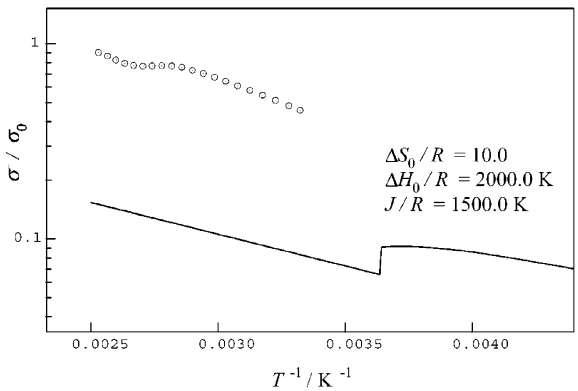

FIGURE 2 Arrhenius plot of electrical conductivities and the simulation curve.

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