Magnetic and Thermal Properties of Crystals Including Isolated Clusters. II. Heat Capacity of $Co_3(C_5H_5)_3S_2$ from 15 to 270 K and Mechanism of Phase Transition[1]

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Heat capacity of $Co_3(C_5H_5)_3S_2$ was measured between 15 and 270 K. A phase transition was discovered at 192.5±0.1 K with the transition enthalpy and the entropy of 5253.4 J mol^{-1} and 28.894 J K^{-1} mol^{-1}, respectively. The transition entropy is well described as the sum of the configurational entropy of $R\ln 8$ due to cyclopentadienyl rings and the magnetic contribution of $R\ln 4$. The transition behavior is satisfactorily accounted for in the whole temperature region investigated in terms of the cooperative coupling between the orientational motion of the rings and the electronic states of a molecule on the basis of the Chesnut exciton model modified by the present authors. The model proposed here is to take both the temperature dependences of the energy parameters and the inversion of the spin state at higher temperatures into account. The measurements of infrared spectra and proton magnetic resonance were made as a function of temperature. These results are favorable to the present model. The electron spin resonance experiment also confirmed the present model.

In the course of our systematic magnetic and thermal investigations of isolated clusters, we reported, as series I,[2] the magnetic interaction of a trinuclear complex compound, $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$, which is one of the typical coordination compounds of the Werner-type with the spin quantum number of 3/2 per each Cr^{3+} ion. In this paper we will deal with magnetic and thermal properties of a trinuclear organometallic compound, $Co_3(C_5H_5)_3S_2$ [tris-(π-cyclopentadienylcobalt) disulfide].

Crystalline $Co_3(C_5H_5)_3S_2$, which was newly synthesized by two of the present authors (T.Y. and S.O.) and others,[3] consists of discrete molecules with the configuration shown in Fig. 1. The cobalt and sulfur atoms form a regular trigonal bipyramid with the cyclopentadienyl rings stereochemically disposed about the cobalt atoms such that lines passing from the center of the equilateral cobalt triangle through the cobalt atoms intersect the centroids of the cyclopentadienyl rings.[4] The magnetic susceptibility measured by two of the present authors (T.Y. and S.O.) and others[4] showed a maximum at 215 K. Above this temperature the susceptibility obeyed the Curie-Weiss law, but below 215 K it decreased rapidly reaching near zero at about 130 K. The effective magnetic moment μ_{eff} calculated from the susceptibility was found to be independent of temperature above 215 K and the average value of μ_{eff} was 2.53 B.M. Below this temperature, however, the μ_{eff} decreased gradually to zero at about 130 K. From the comparison of these values with the theoretical ones based on the orbital-quenched model and also from the simple molecular orbital treatment, it was proposed[4] that the magnetic property of the present compound may be explained by a ground singlet state at the low temperatures followed by a thermally accessible triplet state above 215 K.

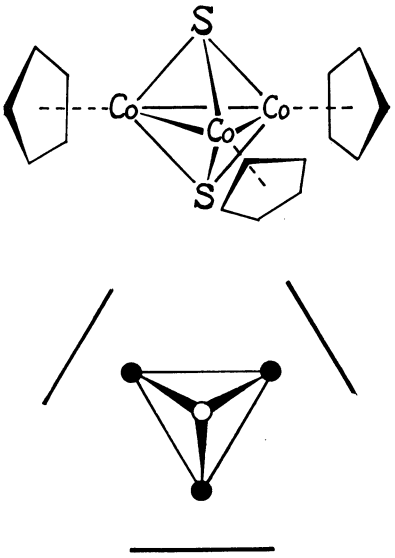

Fig. 1. Molecular configuration of $Co_3(C_5H_5)_3S_2$ (after Ref. 4).

The susceptibility maximum at about 215 K is suggestive of some cooperative effects in the present crystal. It should be, however, remarked here that unlike the preceding salt, $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$, the direct covalent bonds are formed among three metal atoms within a cluster and hence the cobalt atoms do not exist as ionic states in the present compound. The study of the magnetism accompanied by electronic excitation is somewhat difficult compared with that of the magnetism only due to spin states. The cooperative effects in such a system have not been fully investigated. One of the scare examples is the phenomenological theory for some dense magnetic excition systems by Chesnut,[5] who described successfully the gross aspects of the observed anomalous behaviors in some

1) A part of this paper was read at the 5th Japanese Calorimetry Conference, Osaka, (November, 1969), and at The Symposium on Magnetochemistry, Nagoya, (May, 1970).

2) M. Sorai, M. Tachiki, H. Suga, and S. Seki, *J. Phys. Soc. Jap.*, **30**, 750 (1971).

3) S. Otsuka, A. Nakamura, and T. Yoshida, *Liebig's Ann.*, **719**, 54 (1968).

4) S. Otsuka, T. Yoshida, and N. Kamijo, to be published.

5) D. B. Chesnut, *J. Chem. Phys.*, **40**, 405 (1964).

organic free-radical salts in terms of the relatively high exciton concentrations.

The purposes of the present paper are to measure the heat capacity and the related properties between 15 and 270 K and to clarify whether any cooperative phenomenon does exist or not in the present cluster system. As a result a heat capacity anomaly was discovered at 192.5 K with a large amount of the transition entropy unexpected solely from the magnetic contribution due to the old energy schemes.[4]

In order to get more insight into the mechanism of the phase transition we gave attention to the motional behavior of the cyclopentadienyl rings in a crystalline state. The physical properties of ferrocene, $Fe(C_5H_5)_2$, are favorably compared with those of the present crystal.

The transition behavior is satisfactorily accounted for in terms of the cooperative coupling between the orientational motion of the cyclopentadienyl rings and the electronic states on the basis of the Chesnut exciton model modified by the present authors.

Experimental and Results

Material. The present substance was prepared by the method[3] previously described and was recrystallized from a mixture of benzene and *n*-hexane to give dark prism crystals. The results of elementary analysis have been shown in the previous paper.

Heat Capacity. The heat capacity of $Co_3(C_5H_5)_3S_2$ crystal was measured by an adiabatic calorimeter[6] in the temperature range from 15 to 270 K. The

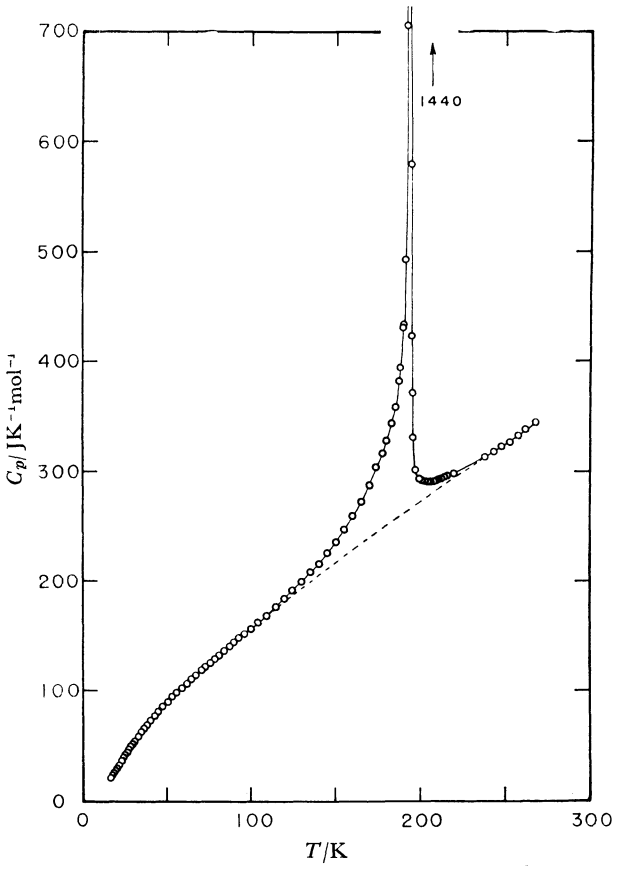

Fig. 2. The heat capacity of $Co_3(C_5H_5)_3S_2$ in the region from 15 to 270 K. Broken line indicates the "normal" heat capacity.

Table 1. The heat capacity of $Co_3(C_5H_5)_3S_2$ (Molecular weight 436.214).

T/K	C_p/JK^{-1} mol^{-1}	T/K	C_p/JK^{-1} mol^{-1}
Series I		160.296	259.865
213.544	293.606	165.370	273.152
215.951	294.697	169.764	287.221
219.856	297.436	174.051	303.801
		177.539	316.756
Series II		180.259	327.912
185.309	357.759	183.255	343.784
187.474	382.292		
189.897	431.324	Series V	
191.811	929.362	17.029	22.1788
193.338	848.175	17.657	24.0802
195.380	371.192	18.483	25.9588
197.666	301.046	19.452	28.4410
199.738	292.799	20.609	31.2609
201.820	291.226	21.878	34.4571
203.904	290.016	23.170	36.8831
205.987	289.981	24.342	40.0600
208.066	290.834	25.497	42.8414
210.140	291.676	26.651	44.8109
212.209	293.064	27.734	47.1279
		28.800	49.5101
Series III		29.927	51.9524
188.310	394.203	31.387	55.0027
190.162	435.352	33.104	58.7891
191.034	492.959	34.883	62.6953
191.641	705.223	36.644	65.9243
192.101	1216.80	38.404	69.1450
192.453	1437.31	40.381	72.9737
192.806	1207.14	42.545	76.6794
193.238	837.818	45.002	80.7959
193.788	578.937	47.733	84.9140
194.637	422.935	50.515	89.3507
195.992	331.177	53.268	93.6470
		56.038	97.7208
Series IV		58.900	102.198
81.181	133.192	61.701	106.352
83.568	136.611	64.509	110.780
86.451	140.529	67.334	114.760
89.497	144.640	70.155	118.413
92.645	148.511	72.981	121.545
95.945	151.914	75.896	124.630
99.755	157.117	78.539	128.206
104.368	163.035	81.149	131.951
109.281	169.431	83.321	138.521
114.313	176.733		
119.464	184.335	Series VI	
124.602	191.964	238.139	313.668
129.731	199.776	243.121	317.760
134.948	208.034	248.056	322.745
140.210	216.846	252.913	327.113
145.312	226.251	257.696	332.644
150.304	236.067	262.434	337.779
155.109	246.728	267.904	343.630

6) T. Matsuo, H. Suga, and S. Seki, *J. Phys. Soc. Jap.*, **30**, 785 (1971).

calorimeter cell contained 11.0344 g (=0.0252958 moles) of the sample and a small amount of helium gas to aid in heat transfer. As this substance is thermally stable but sensitive to air, all treatments were carried out in a dry-box under a stream of dried nitrogen gas.

The results of heat capacity measurements are summarized in Table 1 and plotted in Fig. 2. As can be seen from the figure at heat capacity anomaly was discovered reproducibly at 192.5 ± 0.1 K. This phase transition may be nonisothermal or of second-order because the time required for thermal equilibration after an energy input was not affected by the transition phenomenon. The heat capacity peak is very sharp in the vicinity of the transition point but the tail of excess heat capacity extends down to rather low-temperature side. It is therefore difficult to determine uniquely the enthalpy and the entropy of transition. A dashed line indicated at the base of the transition peak in Fig. 2 is a tentative but plausible curve which separates the excess heat capacities from the overall ones. The enthalpy and the entropy of transition calculated by use of this "normal" heat capacity were found to be 5253.4 $J\,mol^{-1}$ and $28.894\,JK^{-1}mol^{-1}$, respectively.

One of the most interesting features of this crystal that has come to light in the present thermal study is the large amount of transition entropy. The detailed discussions will be given in the next section where the entropy will be related to the mechanism of phase transition.

Infrared Absorption Spectra. The infrared absorption spectra of this substance were obtained by a Grating-type Infrared Spectrophotometer Model DS-402G (Japan Spectroscopic Co., Ltd.) in the range between 4000 and 400 cm^{-1} and by a Spectrophotometer No. FIS-001 (Hitachi Ltd.) in the range from 500 to 80 cm^{-1} at the temperatures of 295 and 120 K, respectively. For the sake of comparison the infrared spectra of ferrocene were also recorded on the same spectrophotometers. The nujol mull method was employed for the preparation of the samples.

In Figs. 3 and 4 the far-infrared spectra of $Co_3(C_5H_5)_3S_2$ and $Fe(C_5H_5)_2$ crystals are shown respectively in the range from 500 to 80 cm^{-1}. In both crystals many new absorption peaks were observed below each phase transition point.

Proton Magnetic Resonance. The proton magnetic resonance absorption spectra of the present substance

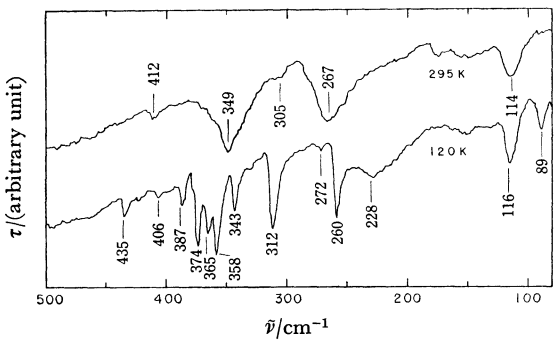

Fig. 3. The far-infrared spectra of $Co_3(C_5H_5)_3S_2$ in the region from 500 to 80 cm^{-1} at the temperatures of 295 and 120 K, respectively.

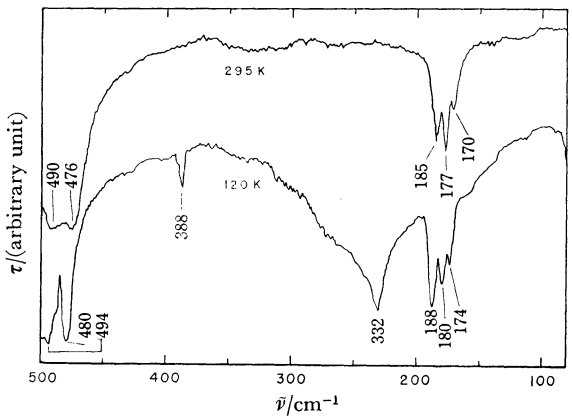

Fig. 4. The far-infrared spectra of $Fe(C_5H_5)_2$ in the region from 500 to 80 cm^{-1} at the temperatures of 295 and 120 K, respectively.

were obtained at a frequency of 21.4 MHz with a broad-line NMR Spectrometer Type BL-1 No. 2004 (Japan Electron Optics Laboratory Co., Ltd.) at 77 K and at room temperature.

The absorption peaks were symmetrical on both sides of the first derivative line. The line width changed from 3.1 gauss at 77 K to 2.6 gauss at room temperature. The second moments of the absorption curves obtained graphically were independent of temperature within the experimental errors between 77 K and room temperature. The average value of the second moment was 0.17 gauss[2]. This value is not so accurate because the field modulasion amplitude employed here was rather large. It is, however, conceivable that the motional narrowing takes place already at a temperature as low as 77 K.

Phenomenological Nature of Phase Transition

The phase transition discovered at 192.5 K is obviously associated with some magnetic interactions, as revealed from the magnetic susceptibility measurement.[4] As was mentioned briefly in the preceding section, the entropy of transition has a large value of $28.894\,J\,K^{-1}mol^{-1}$ and cannot be explained solely by the magnetic contribution based on the thermal excitation of electrons in a molecule from a ground singlet state to an excited triplet state. In this energy scheme the magnetic entropy required for thorough excitation of electrons will be at most $R\ln 4$ ($=11.526\,J\,K^{-1}mol^{-1}$).

On the other hand, some insights into the nature of phase transition may be gained from a closer examination of the molecular and the crystal structures of the present substance. According to the results of X-ray diffraction analysis[4] the crystal belongs to the hexagonal system at room temperature. Its unit cell contains two chemical units and the space group is found to be $P6_3/m$ or $P6_3$. It is also indicated that the cyclopentadienyl ring is accurately coplanar. While there is no constraint imposed by crystal symmetry, the molecule itself has a point group symmetry of D_{3h}. This site symmetry may be accounted for by either a free rotation of or by a twofold orientational disorder

of each cyclopentadienyl ring.

It is, however, possible to exclude the case of free rotation in the present crystal as compared with the case of ferrocene crystal. In a gas phase a ferrocene molecule belongs to a symmetry of $D_{\infty h}$ indicating that no appreciable barrier to free or only slightly hindered rotation of the cyclopentadienyl rings exists.[7] According to Dunitz, Orgel, and Rich,[8] however, the D_{5d} configuration of ferrocene found in the solid state must arise from intermolecular interactions, where the repulsive interaction between hydrogen atoms belonging to adjacent molecules plays a dominant role. Edwards, Kington, and Mason[9] measured the heat capacity of ferrocene crystal, which is diamagnetic, and found a phase transition at 163.9 K with a secondary small C_p maximum at 169 K. On the assumption that each cyclopentadienyl ring can take up two orientations in the room temperature phase, one of which may be obtained by a rotation through 36° in the plane of the ring, they successfully accounted for the observed transition entropy of $R\ln 1.89$ as the twofold orientational disorder.

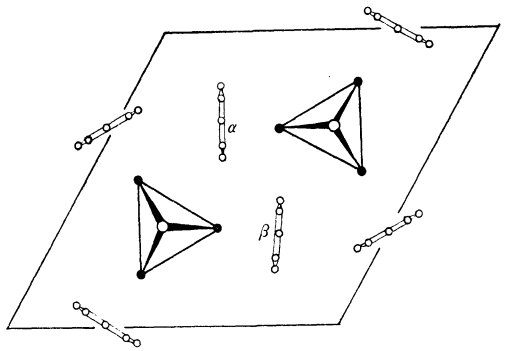

Fig. 5. A projection on the (001) plane of the crystal structure of $Co_3(C_5H_5)_3S_2$ (after Ref. 4).

Similar arguments may be applied to the present crystal, because the packing[4] of cyclopentadienyl rings belonging to different molecules, which are indicated for example as α and β in Fig. 5, has a close resemblance to that of ferrocene crystal along with the *c*-axis. As is the case of ferrocene we assumed that each cyclopentadienyl ring of $Co_3(C_5H_5)_3S_2$ can take up two orientations in the room temperature phase. But the difference from ferrocene is that the present compound has three cyclopentadienyl rings per one molecule. We further assumed that the interactions among three rings belonging to the same molecule would be negligible as each ring is separated far from the other two by a large core of cobalt and sulfur atoms. On these assumptions the number of energetically equivalent configurations attainable for one molecule may be eight ($=2^3$) and the configurational entropy due to the order-disorder phenomenon of the cyclopentadienyl rings amounts to $R\ln 8$. The observed transition entropy of 28.894 JK^{-1} mol^{-1} is satisfactorily explained by the sum of this configurational entropy of $R\ln 8$ and the magnetic contribution of $R\ln 4$, which gives the value of 28.815 JK^{-1} mol^{-1}.

Strong evidences for the assumption that the ordering processes of cyclopentadienyl rings may be concerned in the phase transition can be obtained from the measurements of proton magnetic resonance and infrared spectra of this crystal as a function of temperature. As was mentioned in the previous section, the proton magnetic resonance of the present compound showed the motional narrowing already at a temperature as low as 77 K. And this fact is favorably compared with the case of ferrocene crystal[10] where the motional narrowing also takes place at 77 K and the activation energy for the reorientation is found to be as low as 2.3 kcal mol^{-1}. On the other hand, many new absorption peaks were observed in the infrared spectra of both the present substance and ferrocene below each phase transition point (see Figs. 3 and 4). Although we have not yet completed the assignments to these new peaks, it is likely that they are arising from fundamental and/or lattice bands due to some ordering processes of cyclopentadienyl rings below each phase transition point.

Modified Exciton Theory

In order to make more quantitative arguments about the mechanism of phase transition the phenomenological theory by Chesnut[5] based on the exciton model will be applied directly to the present system in the first half of this section, and in the latter half we will modify this exciton model to achieve the closest agreement between theory and experiment.

According to Chesnut[5] we imagine a system of N molecules, n of which are excited to a triplet state of energy $\varepsilon_0>0$. The mobile excited states will be referred to hereafter as "particles" and the system will be described as one with a particle (exciton) density $\rho=n/N$. The particle entropy of the system may be written as

$$\sigma/Nk = \rho\ln 3 - \rho\ln\rho - (1-\rho)\ln(1-\rho), \qquad (1)$$

and for the Helmholtz energy of the system Chesnut proposed the form as

$$A/N = \varepsilon_0\rho + \frac{1}{2}\varepsilon_1\rho^2 - kT[\rho\ln 3 - \rho\ln\rho - (1-\rho)\ln(1-\rho)], \qquad (2)$$

where $\varepsilon_0\rho$ represents the sum of the single-particle energies and the additional term quadratic in ρ may be attributable to an effective particle-particle interaction. The equilibrium value of ρ, which is obtained by minimizing A with respect to ρ, satisfies the following condition,

$$\rho = \left[\frac{1}{3}\exp(\varepsilon_0+\varepsilon_1\rho)/kT+1\right]^{-1}. \qquad (3)$$

The solution(s) of Eq. (3) must subject to another minimum condition,

$$\frac{1}{N}\frac{\partial^2 A}{\partial\rho^2} = \varepsilon_1 + \frac{kT}{\rho(1-\rho)} > 0. \qquad (4)$$

7) E. A. Seibold and L. E. Sutton, *J. Chem. Phys.*, **23**, 1967 (1955).

8) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).

9) J. W. Edwards, G. L. Kington, and R. Mason, *Trans. Faraday Soc.*, **56**, 660 (1960).

10) L. N. Mulay and A. Attalla, *J. Amer. Chem. Soc.*, **85**, 702 (1963).

On the other hand, the triplet excitation density ρ may be determined from the succeptibility measurement by using the following relation,

$$\chi = \frac{2Ng^2\mu_B^2}{3kT}\left[\frac{1}{3}\exp\left(\Delta E_{eff}/kT\right)+1\right]^{-1} \quad (5)$$

and

$$\rho = \left[\frac{1}{3}\exp\left(\Delta E_{eff}/kT\right)+1\right]^{-1}, \quad (6)$$

where ΔE_{eff} is the effective energy gap between the singlet and the triplet state, g the elctron g-factor and μ_B the Bohr magneton. The temperature dependence of ΔE_{eff} is obtainable from Eqs. (3) and (6);

$$\Delta E_{eff} = \varepsilon_0 + \varepsilon_1\rho. \quad (7)$$

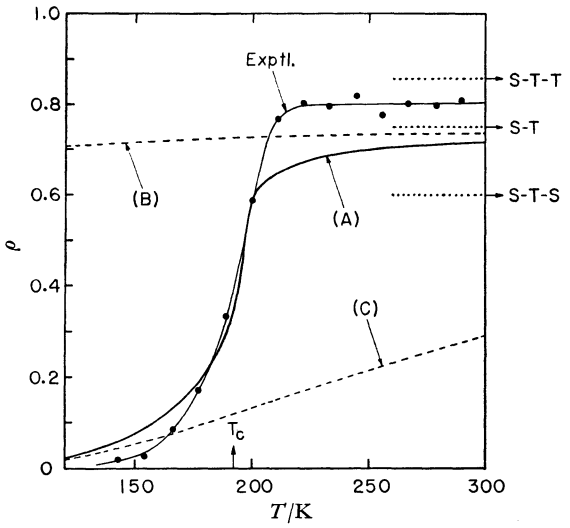

Fig. 6. Observed (curve drawn through black dots) and calculated values of the exciton density *versus* temperature for $Co_3(C_5H_5)_3S_2$. The values of energy parameters ε_1 and ε_0 used for the curves (A), (B), and (C) are indicated in the text.

The exciton density calculated from the succeptibility[4] of the present crystal is compared in Fig. 6 with the theoretical ones derived from Eq. (3). Curve (A) in this figure is corresponding to the best fit, the parameters of which were determined by trials and errors to be ε_0=0.05140eV and ε_1=−0.06559eV. Curves (B) and (C) are the ones in which the attractive interaction between particles is neglected; *i.e.*, ε_0=0.05140eV and ε_1=0 for curve (B) and ε_0=0.00221eV and ε_1=0 for curve (C). These two curves do not account for the experimental one at all. Three horizontal dotted lines indicated at the right-hand-side in Fig. 6 with the symbols *S*-*T*, *S*-*T*-*T* and *S*-*T*-*S* are respectively the limiting values of ρ in the case of $kT\to\infty$, where *S* means a singlet state, *T* a triplet state and a sequence of energy states are indicated as ground state - first excited state - second excited state.

In Fig. 7 the entropy of phase transition is compared with this model. The magnetic contribution estimated from Eq. (1) and the curve (A) in Fig. 6 exceeds the experimental entropy below about 165 K and hence the configurational entropy becomes negative below this temperature. We cannot accept such a feature from a physical reality.

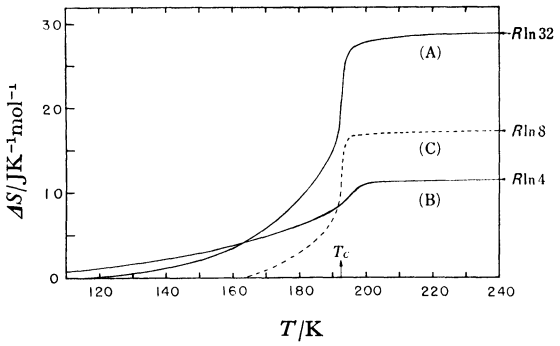

Fig. 7. The entropy of phase transition *versus* temperature for $Co_3(C_5H_5)_3S_2$. Curve (A) is the experimental value obtained from the heat capacity measurement. Curve (B) is the magnetic contribution calculated from Eq. (1) and the curve (A) in Fig. 6. Curve (C) is the configurational entropy determined by subtracting the value of curve (B) from that of curve (A) at respective temperature.

Apart from the details, however, this model is able to describe the gross aspects of the observed magnetic behavior. Then we attempt to modify this exciton model so that the closest agreement may be obtainable. As to the Chesnut model the energy parameters ε_1 and ε_0 are assumed to be independent of temperature. But this is not the case because a real system will be affected by thermal expansion. Moreover, the exciton density ρ determined from the experiment exceeds above near 208 K the limiting value of 0.75 based on the energy scheme of a ground singlet state followed by an excited triplet state (see Fig. 6). This feature may be interpreted either by considering a system with additional multi-degenerate state(s) above the first excited state such as *S*-*T*-*T* or by inverting the degeneracy of a ground and an excited state above 208 K. The latter model based on the inversion in the spin state seems to be more favorable to the present system as will be mentioned in the next section.

We modify the Chesnut exciton theory so as to take account of both a temperature dependence of the energy parameters and the inversion in the spin state above 208 K. In this model one of the energy parameters is eliminated by the condition: When ρ=3/4, $\Delta E_{eff}=\varepsilon_0(T)+\rho\varepsilon_1(T)=0$, then

$$\left.\begin{aligned}\varepsilon_0(T) &= -3\varepsilon_1(T)/4\\ \text{and}\qquad \Delta E_{eff} &= \varepsilon_1(T)\left(\rho-\frac{3}{4}\right).\end{aligned}\right\} \quad (8)$$

The temperature dependences of ε_1 and ε_0 were obtained by fitting Eqs. (3) and (8) to the experimental values of ρ. The results are shown in Fig. 8. Appreciable but different temperature dependences were found below and above the transition point. The following linear dependences were assumed:

$$\varepsilon_1/k = \begin{cases}184.0 - 6.471T & (T > T_c),\\ -1626 + 4.4T & (T < T_c).\end{cases} \quad (9)$$

On this assumption the temperature dependence of the exciton density except for the vicinity of the transition point is satisfactorily accounted for (see Fig. 9). As is shown in Fig. 10, the transition entropy obtained from

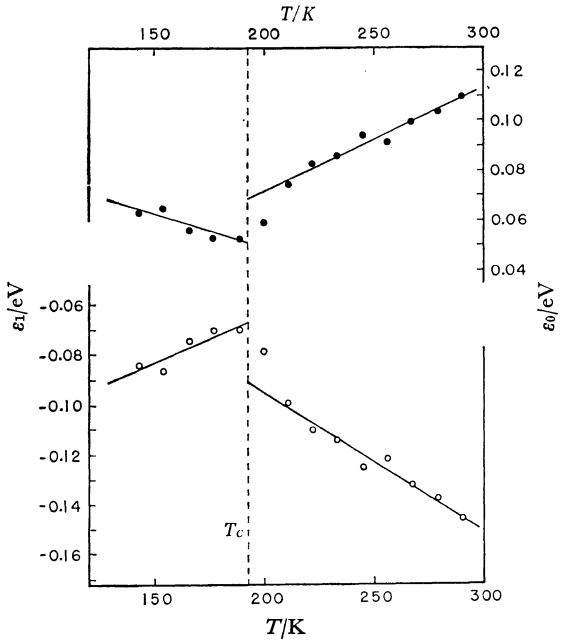

Fig. 8. The temperature dependences of the energy parameters ε_1 and ε_0 for $Co_3(C_5H_5)_3S_2$. Open and solid circles are the observed values. The straight lines are formulated in Eq. (9).

our heat capacity measurement is also well explained in the whole temperature region as the sum of the magnetic contribution derived from the present model and the configurational entropy due to the cyclopentadienyl rings. The effective energy gap ΔE_{eff} between a singlet and a triplet state is shown in Fig. 11 as a function of temperature. As can be seen from this figure, consideration of temperature dependence of the energy parameters well accounts for the actual behavior.

We have so far regarded the dominant origin of the

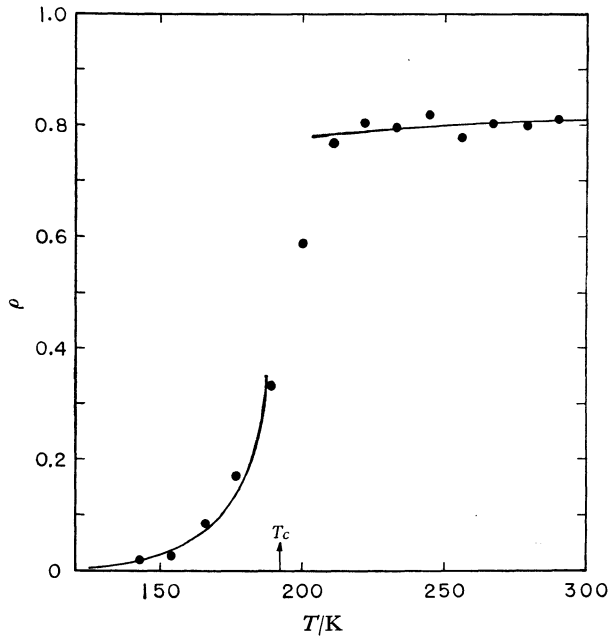

Fig. 9. Comparison of the exciton density between the observed (solid circle) and the calculated values (solid lines) based on the present model.

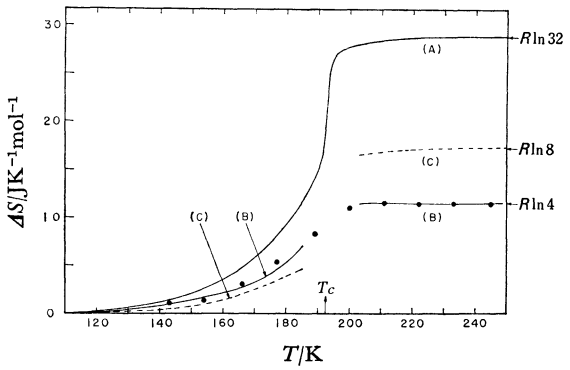

Fig. 10. The entropy of phase transition *versus* temperature for $Co_3(C_5H_5)_3S_2$. Curve (A), the experimental value determined from the heat capacity measurement; Curve (B), the magnetic contribution calculated based on the present model; Curve (C), the configurational entropy corresponding to the (A—B); Solid circle, the observed magnetic entropy determined from the magnetic susceptibility measurement.[4]

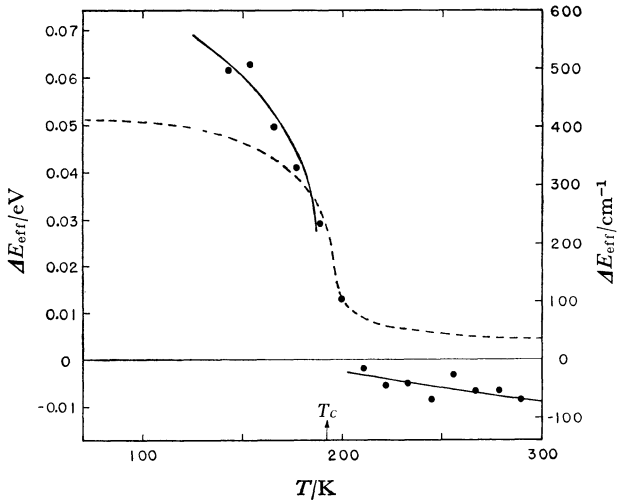

Fig. 11. Effective excitation energy ΔE_{eff} as a function of temperature for $Co_3(C_5H_5)_3S_2$. Solid circle, the observed value calculated from the susceptibility data;[4] Solid line, the theoretical value based on the present model; Broken line, the theoretical value based on the Chesnut exciton model.

temperature dependence of ε_1 and ε_0 as existing thermal expansion of real crystal but a remarkable difference in temperature dependence between both sides of the transition point will be a further problem.

Mechanism of Phase Transition

In this section we will present a physical picture for the temperature dependence of ΔE_{eff} and also for the inversion of spin state. In doing this, it is convenient to make arguments based on the electronic configuration of the present cluster molecule[4] and that of the nickel congener,[11] $Ni_3(C_5H_5)_3S_2$, derived from a simple molecular orbital scheme.

As we are interested in a relation between the electronic state and the spin state, our discussion will be

11) H. Vahrenkamp, V. A. Uchtman, and L. F. Dahl, *J. Amer. Chem. Soc.*, **90**, 3272 (1968).

confined to four truncated anti-bonding orbitals involved in the 3*d* orbitals of the cobalt atoms. According to Otsuka *et al.*,[4] the d_{z^2} orbitals of three cobalt atoms combine to give doubly degenerate anti-bonding orbitals $e'^*(d_{z^2})$, $(2\phi_1-\phi_2-\phi_3)/\sqrt{6}$ and $(\phi_2-\phi_3)/\sqrt{2}$. Here, ϕ_i is the d_{z^2} orbital of the *i*th cobalt atom and the coordinate axes at each cobalt atom are so chosen that the *z*-axis points to the centroid of the equilateral cobalt triangle, the *x*-axis lies in the triangle plane and the *y*-axis completes right-handed coordinate system. Similarly the $d_{x^2-y^2}$ orbitals give rise to two anti-bonding orbitals $e'^*(d_{x^2-y^2})$. The d_{xy} and the d_{zx} orbitals bring about non-degenerate anti-bonding orbital $a_1''^*(d_{xy})$ and $a_2'^*(d_{zx})$, respectively. Of all the valence electrons only eight electrons are accomodated in these anti-bonding orbitals. While it is not possible to settle the relative energy levels among these orbitals beyond the point of speculation, Otsuka *et al.* suggested that the configuration in the ground state will be $e'^*(d_{x^2-y^2})^4$, $e'^*(d_{z^2})^4$ leaving $a_1''^*(d_{xy})^0$ and $a_2'^*(d_{zx})^0$ vacant. Here, the superscript indicates the number of electrons accomodated in each anti-bonding orbital. Although their qualitative approach does not tell which orbital comes higher among the e'^* orbitals or among $a_1''^*$ and $a_2'^*$ orbitals, this energy scheme does not conflict with the gross aspect of magnetic behavior and with the bonding scheme[11] in the nickel congener.

It should be noticed here that the phase transition in the present crystal is satisfactorily accounted for by the sum of both configurational and magnetic contribution, the cooperative effect obviously arises from the gear-motion of cyclopentadienyl rings in the lattice. As was pointed out by Chesnut,[5] no cooperative phase transition may result in such a magnetic system as the present crystal where a discontinuity is not observed in the magnetic susceptibility curve. It is, however, possible to suppose that a cooperative coupling is still present between rotational motion of the cyclopentadienyl rings and the electronic state of a molecule. The existence of such a cooperative coupling is secured by the fact that the magnetic behavior can only be explained by varying the energy gap ΔE_{eff} with temperature and by introducing the inversion of spin state at higher temperatures.

We propose the following energy schemes as is shown in Fig. 12: (1) The energy levels of the $e'^*(d_{x^2-y^2})$ and the $a_1''^*(d_{xy})$ orbitals will not depend on temperature as the orbital overlap between these and the π-orbitals of each cyclopentadienyl ring is negligible. (2) The $e'^*(d_{z^2})$ level is also nearly independent of temperature. Although the small overlap exists, the reorientational motion of the ring will scarcely affect the energy state of this orbital because the overlapping is nearly symmetrical around each *z*-axis. (3) The $a_2'^*(d_{zx})$ will be sensitive to the motional behavior of the ring. Frequent reorientation of the ring would lead to almost complete smearing of the electron density around the circle formed by the rotating group. Hence the energy of this orbital will decrease with increasing reorientational motion of the ring. (4) The level-crossing is assumed to take place between the $a_2'^*(d_{zx})$ and the $e'^*(d_{z^2})$ at a certain temperature T^* and thus the inversion of spin state occures above T^*. In the present crystal the value of T^* is 208 K which is slightly higher than the phase transition point. Favorable evidence for the inversion of spin state is also obtained from the preliminary experiment of electron paramagnetic resonance by Kuwata,[12] who measured the absorption intensity and the line width as a function of temperature. (5) The physical meaning of ΔE_{eff} differs

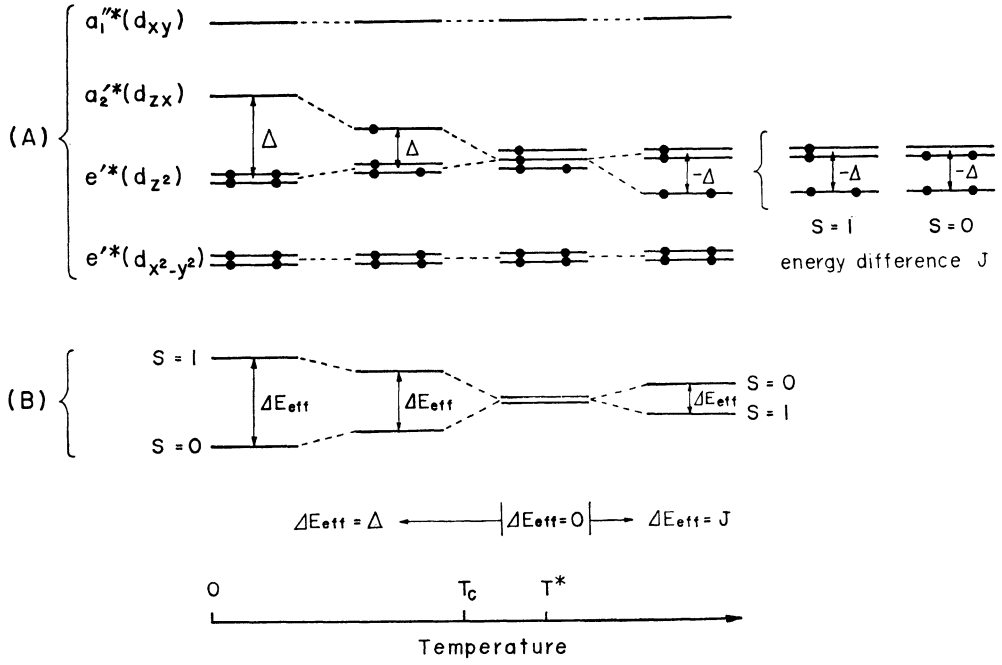

Fig. 12. Temperature dependence of (A) the electronic and (B) the spin states for $Co_3(C_5H_5)_3S_2$. The meanings of the molecular orbital symbols corresponding to each irreducible representations are indicated in the text.

12) K. Kuwata: private communicatoin (to be published).

from each other below and above T^*. ΔE_{eff} is equivalent to the level-spacing between the ground and the excited electronic states below T^*. Above T^*, on the other hand, ΔE_{eff} corresponds to the intra-J based on Hund's rule. The intra-J is in general almost independent of temperature. This fact really coincides with the present result as is shown in Fig. 11.

Conclusion

In the preceding sections of this paper we have shown the possibility of explaining the observed phase transition phenomenon of $Co_3(C_5H_5)_3S_2$ crystal based on the cooperative coupling between reorientational motion of the cyclopentadienyl rings in the lattice and the electronic state of a molecule. Magnetic behavior can be well described by introducing both the temperature dependences of the energy paramaters (ε_1 and ε_0) and the inversion of spin state at higher temperatures to the excition model derived by Chesnut.

Although the present model does not conflict with the existing experimental results, a possible model including the effects of higher excited states is still remaining. More rigorous calculation of molecular orbitals is necessary to gain more quantitative insight into the electronic state of the present crystal.

Heat capacity measurement of the nickel congener $Ni_3(C_5H_5)_3S_2$, will provide a useful information to judge the validity of the present arguments. Molecular and crystal structures of this compound are isomorphous with the present substance. This molecule, however, contains three more electrons compared with $Co_3(C_5H_5)_3S_2$ to give one unpaired electron in the ground electronic state.[11] So far as the energy scheme shown in Fig. 12 is adopted, anomalous magnetic behavior will not be expected for the nickel compound except for weak intercluster interactions. Even if a phase transition be observed in the nickel compound, such a phase transition would result solely from a configurational effect of cyclopentadienyl rings and the transition entropy would amount to only $R\ln 8$.

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