Thermochimica Acta, 109 (1986) 29–44
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRIC STUDIES ON PHASE TRANSITIONS ARISING FROM ORIENTATIONAL ORDER–DISORDER OF THE MOLECULAR AXES OF FERROCENE AND ITS DERIVATIVES *

MICHIO SORAI and YUTAKA SHIOMI **

Chemical Thermodynamics Laboratory, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

(Received 22 July 1986)

ABSTRACT

Heat capacities of the channel inclusion compound, $Fe(C_5D_5)_2 \cdot 3(NH_2)_2CS$, and two ferrocenium salts, $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$ and $[Fe(C_5H_5)_2]^+(PF_6)^-$, have been measured with adiabatic calorimeters between 13 and 393 K. Five phase transitions were found for $Fe(C_5D_5)_2 \cdot 3(NH_2)_2CS$ corresponding to those for $Fe(C_5H_5)_2 \cdot 3(NH_2)_2CS$. The dominant phase transitions at 145.8 and 160.6 K are responsible for the onset of reorientational order–disorder of the molecular axis of $Fe(C_5D_5)_2$ in the clathrate cavity. The mass-effect of the guest ferrocene molecule on the phase transitions was not remarkable. The ferrocenium salt, $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$, exhibited four phase transitions and two glass transition phenomena at low temperatures while its analog, $[Fe(C_5H_5)_2]^+(PF_6)^-$, brought about only three phase transitions without showing the glass transition. The higher-temperature phase transitions in these two salts have been assigned to the reorientational order–disorder mechanism of the molecular axes of the cations in the pseudo-cavities formed by eight PF_6^- anions. For the origin of the lower-temperature phase transitions in these two salts, three possibilities have been discussed. Among them, plausible origin is likely to be an order–disorder change of PF_6^- anion in the lattice. An important unsettled problem common to these three compounds is a question whether or not the $Fe(C_5D_5)_2$ and the cations, $[Fe(C_5H_5)(C_6H_6)]^+$ and $[Fe(C_5H_5)_2]^+$, are still reorienting around their molecular axes even at the lowest-temperature phase.

INTRODUCTION

Phase transition is a classical subject having a long history of studies but the matter is still up-to-date. On one hand many novel phase transitions

---

* Contribution No. 109 from the Chemical Thermodynamics Laboratory. This paper has been dedicated to Emeritus-Professor Syûzô Seki, a member of the Japan Academy, in honor of his great contribution to calorimetry and thermal analysis. One of the present authors (M.S.) began to study chemical thermodynamics in 1961 under his guidance and learnt from him much of what he knows about it today.

** Present address: Sumitomo Chemical Co., Ltd., Konohana-ku, Osaka 554, Japan.

0040-6031/86/$03.50

have been experimentally discovered and on the other hand unsettled problems have been successfully interpreted by the current theories. Even if the subject is confined to phase transitions arising from orientational order–disorder phenomena in a crystalline state, a variety of phase transitions exist [1]. This paper is concerned with phase transitions characterized by molecular motions, in particular orientational order–disorder of molecular axes, of ferrocene and its derivatives in the crystal lattices.

Ferrocene, bis(η^5-cyclopentadienyl)iron(II): $Fe(C_5H_5)_2$, is a representative or key-substance of organometallic compounds with the sandwich-type structure. Owing to its unusual molecular form ferrocene has attracted many investigators' attention ever since its first synthesis in 1952 [2,3]. The thermodynamic properties of the ferrocene crystal were first studied by Edwards et al. in 1960 [4,5] on the basis of heat capacity measurements. They found a λ-type phase transition at 163.9 K with a small subsidiary peak at 169 K. They attributed this transition to rotational disorder of the π-cyclopentadienyl rings in the high-temperature phase. This phase transition is nowadays known to occur between the triclinic low-temperature (LT) phase and the monoclinic high-temperature (HT) phase [4,6–10]. This well-known λ-type transition was, however, revealed to take place between two metastable phases by Ogasahara et al. in 1979 [11,12]. They found a stable low-temperature phase which was transformed into the monoclinic HT-phase via a first-order phase transition at 242 K. This stable LT-phase was soon found to belong to an orthorhombic system [13,14]. Furthermore, ferrocene is known to exhibit an interesting crystal-disintegration below the λ-point, which is an independent phenomenon from the λ-type phase transition [4,11,12,15]. On cooling a single crystal of ferrocene, crystal disintegration occurs with explosive violence accompanied by evolution of heat. The disintegration energy, determined by temperature-jump calorimetry [16], was so large as to exceed the enthalpy associated with the λ-transition. Both the crystal polymorphism and the disintegration phenomenon were likewise observed for deuterated ferrocene, ferrocene-d_{10} [17,18]. These characteristic features of the ferrocene crystal seem to have their origin in an uncommon five-fold molecular symmetry. As easily supposed, molecules having such a symmetry are hard to settle in a crystal lattice while keeping a long-range periodicity, including the position of H atoms.

This type of "incommensurability" might also be encountered in channel inclusion compounds accommodating ferrocene as their guest and in ferrocenium compounds which have been studied in the present paper. In the case of a ferrocene–thiourea clathrate compound, thiourea forms a hexagonal channel lattice in each cavity of which a single molecule of ferrocene is housed as a guest [19]. Gibb [20] found an unusual temperature-dependent relaxation of the electric field gradient tensor for this compound on the basis of ^{57}Fe Mössbauer spectroscopy. This so-called "electric-quadrupole relaxation" was found to be caused by anisotropic reorientation of the ferrocene molecules in the cavities of the clathrate lattice. The molecular axis can lie either parallel or perpendicular to the hexagonal channel axis. Heat capacity measurements have elucidated that the excitation of the molecular reorientation is established through phase transition phenomena [21]. But still unsolved is the problem of how ferrocene molecules with five-fold symmetry can be settled in the hexagonal channel in the lowest-temperature phase. In this paper, the heat capacity of the clathrate compound of ferrocene-d_{10} and thiourea will be described with the primary goal of learning more about the transition mechanism through a mass effect of the guest molecules.

A similar situation occurs in ionic crystals consisting of ferrocenium and its analogous cations. Based on ^{57}Fe Mössbauer spectroscopy, Fitzsimmons and Hume [22,23] observed an electric-quadrupole relaxation for $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$ analogous to the ferrocene–thiourea clathrate compound. According to their model, the organometallic cation is assumed to lie at an eight-coordinate site made up of eight PF_6^- groups and to start reorientational motion at 321 K. Here we also encounter the "incommensurability" problem of the cation in the "tetragonal" lattice formed by PF_6^- anions. The $[Fe(C_5H_5)(C_6H_6)]^+$ cation no longer has a symmetry axis. These unfavorable cations having five- and six-membered rings, however, must be regularly arranged in the low-temperature "tetragonal" phase while keeping a long-range periodicity if the compound is to obey the third law of thermodynamics. We expected that we would be able to gain some insight into the molecular arrangement in the low-temperature phase if we studied this system from a calorimetric or entropic viewpoint. To this end, heat capacity measurements have been made in this paper for this compound. A calorimetric study has also been made on $[Fe(C_5H_5)_2]^+(PF_6)^-$ for comparison. In this case, the situation seems to be simpler than that for $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$, because there is no discrimination between the head and tail of the cation.

EXPERIMENTAL

Sample preparation

Ferrocene-d_{10}, used for preparation of the thiourea clathrate compound, $Fe(C_5D_5)_2 \cdot 3(NH_2)_2CS$, was taken from the same batch as previously prepared [17,18]. The isotope purity was better than 99.8%. The clathrate compound was prepared according to a procedure described by Clement et al. [19], except that we used ethanol instead of methanol as the solvent. The product was dried in a dry nitrogen stream for 48 h and then in vacuum for 30 min. Anal. Calcd.: C, 36.79%; D, 7.59%; N, 19.80%; S, 22.66%. Found: C, 36.95%; D, 7.59%; N, 19.79%; S, 22.70%. The stoichiometry of the clathrate, determined by a sublimation method, gave the molar ratio of ferrocene-d_{10} to thiourea as 1 : 3.0107.

(η^6-Cyclohexatriene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate, $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$, was prepared by the method of King [24]. The crude product was recrystallized twice from absolute ethanol. The yellow crystals obtained were dried in vacuum for 48 h at room temperature and then for 24 h at 100°C to remove ethanol solvate molecules occluded in the crystal. Anal. Calcd.: C, 38.41%; H, 3.22%. Found: C, 38.46%; H, 3.25%. Substitution of the C_5H_5-ring by the C_6H_6-ring was examined by ^1H NMR to give a 1 : 1 ratio.

Ferrocenium hexafluorophosphate, $[Fe(C_5H_5)_2]^+(PF_6)^-$, was prepared according to the method of Hendrickson et al. [25]. The crude product was recrystallized from water to give dark green crystallites. The crystals were dried in vacuum for 72 h. Anal. Calcd.: C, 36,29%; H, 3.05%. Found: C, 36.47%; H, 3.08%.

Infrared spectroscopy

Infrared spectra in the range 4000–400 cm^{-1} and far-infrared spectra in the range 400–30 cm^{-1} were recorded for Nujol mulls with an infrared spectrophotometer (Japan Spectroscopic Co., Ltd., Model DS-402G) and with a far-infrared spectrophotometer (Hitachi, Ltd., Model FIS-3).

Polarizing microscopy

The change in optical anisotropy at the phase transition temperatures was observed with a polarizing microscope (Olympus, Model BHA-751-P) equipped with a heating stage (Union Optical Co., Ltd., Model CMS-2).

Heat capacity measurements

Heat capacity measurements were made with an adiabatic calorimeter [26] for $Fe(C_5D_5)_2 \cdot 3(NH_2)_2CS$ in the range 13–300 K and for $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$ and $[Fe(C_5H_5)_2]^+(PF_6)^-$ between 12 and 393 K. A calorimeter cell made of gold-plated copper [12] contained 18.1918 g (or 0.042859 mol) of $Fe(C_5D_5)_2 \cdot 3(NH_2)_2CS$. Another cell made of gold and platinum [27] was used for the heat capacity measurements of $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$ and $[Fe(C_5H_5)_2]^+(PF_6)^-$. The amount of sample was 15.3353 g (or 0.044577 mol) and 20.1931 g (or 0.061006 mol), respectively. A small amount of helium gas was sealed in the cells to aid the transfer of heat.

RESULTS AND DISCUSSION

$Fe(C_5D_5)_2 \cdot 3(NH_2)_2CS$

Calorimetric results were evaluated in terms of C_p, the molar heat capacity at constant pressure. The experimental data are plotted in Fig. 1.

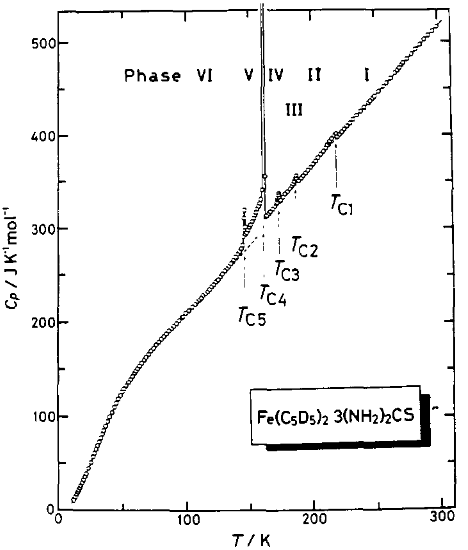

Fig. 1. Molar heat capacities of $Fe(C_5D_5)_2 \cdot 3(NH_2)_2CS$ between 12 and 300 K.

Five well-resolved heat capacity anomalies were found at 145.8, 160.6, 173.4, 187.1 and 219.0 K. These five C_p anomalies just correspond to those observed in $Fe(C_5H_5)_2 \cdot 3(NH_2)_2CS$ [21] except for a slight difference between the respective peak temperatures. As discussed previously [21], these anomalies are associated with phase transitions. In what follows, therefore, the five transition temperatures will be designated as T_{Cn} ($n = 1$, 2, 3, 4 and 5) in order of decreasing temperature. The crystalline phases bounded by T_{Cn} will be named phases I–VI with descending temperature: i.e., phase I is the highest-temperature phase while phase VI corresponds to the lowest-temperature phase.

As in the case of the normal ferrocene–thiourea clathrate compound, the phase transition at T_{C4} of the present compound was the largest transition among the five and showed an undercooling effect characteristic of a first-order phase transition. Although the heat capacity anomaly arising from the phase transition at T_{C5} is not so conspicuous, this phase transition was also found to show an undercooling effect. The thermal relaxation time, the time required for thermal equilibration after an energy input to the calorimeter, was long in the temperature region including T_{C4} and T_{C5}, 145–162 K.

In order to determine the enthalpy and entropy associated with the particular phase transitions, we estimated two normal heat capacity curves, C_p(normal), used for the temperature regions below and above T_{C4}. The C_p (normal) below T_{C4} was determined according to the effective-frequency-distribution method [28] by using the observed heat capacities in the range 12–122 K and the infrared spectra, while the C_p(normal) above T_{C4} corre-

TABLE 1

Enthalpy and entropy of phase transitions in ferrocene–thiourea channel inclusion compounds. The data for the normal ferrocene clathrate have been taken from ref. 21. The figures in square brackets indicate [T_C(ferrocene-d_{10}) − T_C(ferrocene-h_{10})]/K.

Guest	Transition	T_C (K)	$\Delta_{trs}H$ (kJ mol^{-1})		$\Delta_{trs}S$ (J K^{-1} mol^{-1})	
$Fe(C_5D_5)_2$	VI → V	T_{C5}: 145.8 [−1.4]	(0.057)	1.819	(0.39)	11.01
	V → IV	T_{C4}: 160.6 [0.8]	(1.762)		(10.62)	
	IV → III	T_{C3}: 173.4 [2.0]	0.011		0.07	
	III → II	T_{C2}: 187.1 [1.6]	0.031		0.17	
	II → I	T_{C1}: 219.0 [−1.0]	0.057		0.27	
		total	1.918		11.52	
$Fe(C_5H_5)_2$	VI → V	T_{C5}: 147.2	(0.263)	1.737	(1.79)	11.02
	V → IV	T_{C4}: 159.8	(1.474)		(9.23)	
	IV → III	T_{C3}: 171.4	0.014		0.08	
	III → II	T_{C2}: 185.5	0.035		0.19	
	II → I	T_{C1}: 220.0	0.077		0.36	
		total	1.863		11.65	

sponded to a curve smoothly connecting the observed heat capacities in the temperature regions having no phase transition effects. The two C_p (normal) curves brought about a discontinuity at T_{C4} amounting to 10.64 J K^{-1} mol^{-1}. This discontinuity originates from a change in the molar volume [21]. The transition enthalpy and entropy were determined by integration of the excess heat capacities beyond C_p(normal) with respect to T and ln T. The thermodynamic quantities arising from the phase transitions thus obtained are summarized in Table 1. Those for $Fe(C_5H_5)_2 \cdot 3(NH_2)_2CS$ [21] are also shown in Table 1 for comparison. As given in the square brackets in Table 1, the change in phase transition temperatures on replacing the normal ferrocene guest molecule by heavy ferrocene is at most 2 K. This fact suggests a minor role of the mass-effect for the mechanism of the present phase transitions. In other words, instead of the kinetic energy of the guest molecule, the temperature dependence of the potential energy curve due to intermolecular interactions governs the phase transitions.

As in the case of the normal ferrocene clathrate compound, the sum of all the transition entropies (11.52 J K^{-1} mol^{-1}) was basically the same as R ln 4 (= 11.53 J K^{-1} mol^{-1}). As far as we discuss the present phase transitions within the framework of an orientational order–disorder mechanism concerning the guest ferrocene molecules in the thiourea cavities, this fact clearly indicates that there are four energetically nearly-equal orientations in phase I while in phase VI only one orientation of the four is populated. Of the five phase transitions, two lowest-temperature transitions, labeled T_{C4} and T_{C5}, are mainly concerned with the reorientational mechanism of ferrocene-d_{10} molecules in the thiourea host-lattice, as the ^{57}Fe Mössbauer spectroscopy [20], X-ray diffraction analysis [29] and ^{1}H NMR [30] have shown the onset of the reorientational motion around 162 K. According to the X-ray structural work, thiourea molecules form a honeycomb of channels spiraling with a pitch of 120° parallel to the *c*-axis. Within these channels, the site of point symmetry 32 is occupied by the iron atom of the ferrocene molecule. At high temperatures, above 162 K, the cyclopentadienyl rings of a ferrocene molecule are disordered and the time-averaged picture shows regions of three-dimensionally delocalized cyclopentadienyl electron density around the iron atoms. On the other hand, the five-fold axes of ferrocene molecules are frozen in a number of non-equivalent orientations at low temperatures [30]. The ^{57}Fe Mössbauer spectroscopy study has pointed out that the reorientational motion of ferrocene molecules is excited

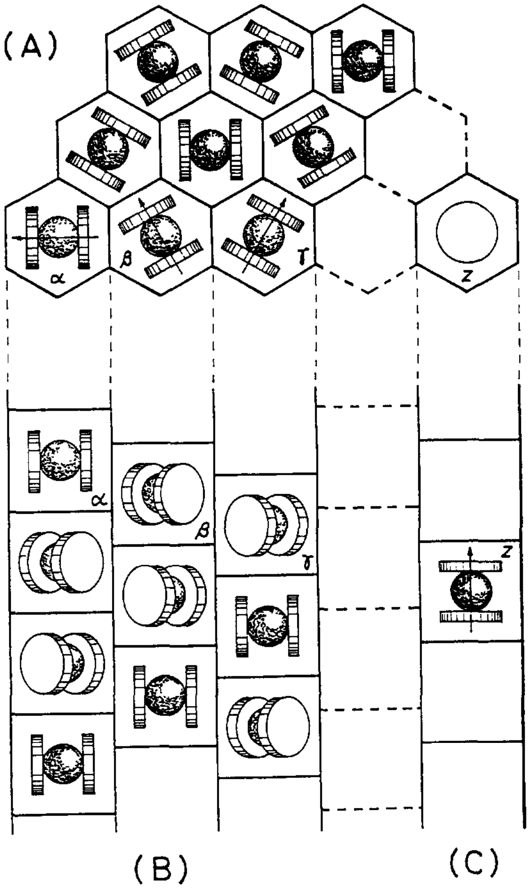

Fig. 2. Schematic drawing showing the relative orientation of the guest ferrocene molecules in the honeycomb channels formed by the thiourea host-lattice. (A) and (B) are the top and side views of the suggested ordered phase.

through two processes: one is a rapid reorientation about the channel axis of those molecules whose axes lie in the plane perpendicular to it and the other is a slow jump between those in the plane and the direction parallel to the channel axis. Taking into account these spectroscopic and structural informations, we can schematically draw possible orientations of the molecular axis of ferrocene in the cavity formed by thiourea host-lattice as shown in Fig. 2. At high temperatures, say, above T_{C4}, ferrocene-d_{10} molecules may be randomly reoriented among the α, β, γ and z-directions. The entropy acquisition due to this kind of reorientation can amount to $R \ln 4$ ($= 11.53$ J K^{-1} mol^{-1}) and well accounts for the transition entropy (11.01 J K^{-1} mol^{-1}) observed for both the phase transitions at T_{C5} and T_{C4}.

Detailed analysis and discussion, in particular the mass effect on heat capacity will be described elsewhere [31].

$[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$

The results of heat capacity measurements are plotted in Fig. 3. Four phase transitions were found at 321.5, 280.2, 265.9 and 158.3 K. We shall designate them T_{C1}, T_{C2}, T_{C3} and T_{C4}, respectively. The crystalline phases will be named as phases I–V with descending temperature. In addition to these phase transitions, glass transition phenomena were observed at around 103 and 138 K in phase V, which have been indicated in Fig. 3 by T_{g2} and T_{g1}. The solid circles in Fig. 3 indicate the heat capacities of the undercooled phase IV. Therefrom, the phase transition at T_{C4} is concluded to be obviously of first order.

The normal heat-capacity curve used below T_{C1} was determined by the effective-frequency-distribution method [28], in which the C_p data used for

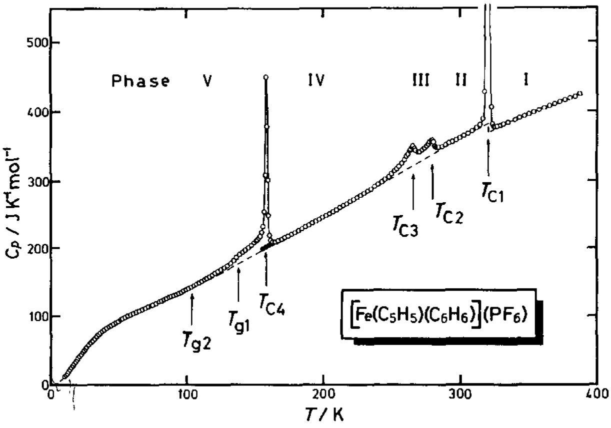

Fig. 3. Molar heat capacities of $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$ between 12 and 393 K. The solid circles indicate the heat capacities of the undercooled high-temperature phase. The broken curve indicates the normal heat capacity.

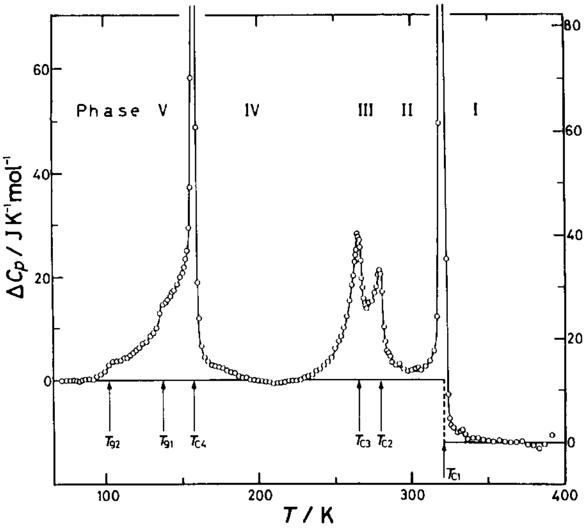

Fig. 4. Excess heat capacities, ΔC_p, arising from the phase transitions of $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$. The discontinuity of two normal heat capacity curves at T_{C1} amounts to 12.1 J K^{-1} mol^{-1}.

the least-square fitting were those in the temperature ranges 10–93 and 186–207 K. On the other hand, the normal heat-capacity curve used above T_{C1} was a simple extrapolation curve from phase I. These two C_p(normal) are shown in Fig. 3 by broken curves. A discontinuity of 12.1 J K^{-1} mol^{-1} appeared at T_{C1} which was taken to be a boundary temperature of two C_p (normal) curves. Figure 4 illustrates the excess heat capacities, ΔC_p, beyond the C_p(normal) curves. Three phase transitions, labeled T_{C1}, T_{C2} and T_{C3}, inseparably overlap one another. We then regarded two phase transitions at T_{C3} and T_{C2} as being a pretransitional phenomenon inherent in the main transition at T_{C1}. The glass-transition phenomena are clearly seen as two-step heat-capacity anomalies below T_{C4}. The residual entropy estimated by extrapolating the equilibrium ΔC_p curve just below T_{C4} down to 0 K amounts to 0.47 J K^{-1} mol^{-1}. Detailed discussion of these glass-transition phenomena will be given elsewhere [32].

The enthalpy and entropy arising from the phase transitions are given in Table 2. The four phase transitions can be classified into two basic groups: one is a lower-temperature phase transition at T_{C4} with two glass transitions in its low-temperature side and the other is a higher-temperature phase transition at T_{C1} with two subsidiary C_p peaks at T_{C3} and T_{C2}. Judging from the good agreement of the present phase transition temperature of T_{C1} = 321.5 K with the critical temperature of 321 K predicted by the ^{57}Fe Mössbauer spectroscopic study by Fitzsimmons and Hume [22,23], the higher-temperature phase transition can safely be concluded to arise from the onset of reorientational motion of the molecular axis of the

TABLE 2

The enthalpy and entropy arising from the phase transitions of $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$

Transition	T_C (K)	$\Delta_{trs}H$ (kJ mol^{-1})	$\Delta_{trs}S$ (J K^{-1} mol^{-1})
Phase V → IV	T_{C4}: 158.3	1.19	8.01
IV → III	T_{C3}: 265.9	4.54	14.55
III → II	T_{C2}: 280.2		
II → I	T_{C1}: 321.5		

$[Fe(C_5H_5)(C_6H_6)]^+$ cation in the framework formed by eight PF_6^- anions. Based on careful analysis of the variable-temperature Mössbauer spectra, they have proposed a transition mechanism responsible for the unusual electric quadrupole relaxation. For ease of understanding, their model is reproduced in Fig. 5. According to their model, the organometallic cation, $[Fe(C_5H_5)(C_6H_6)]^+$, is assumed to lie at an eight-coordinate site made up of eight PF_6^- groups. At low temperatures the molecular axis of the cation is collinear with the *z*-axis of the tetragon. As the temperature is raised, the *x* and *y* orientations are Boltzmann populated, and jump reorientations between *x* and *y* directions take place. These orientations become faster with further temperature increase. Finally, all reorientations are so rapid that the cation is effectively spherical. This brings about a crystallographic change from a tetragonal to a cubic phase at about 321 K. In fact, they have observed that the polarizing colors disappear completely at 319 K under a polarizing microscope, indicating a crystallographic change to cubic symmetry [22,23]. If we accept their reorientational model, the entropy acquisition

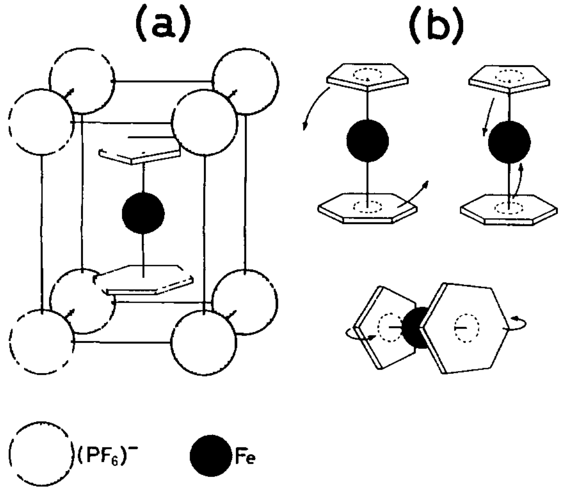

Fig. 5. Schematic representation of (a) the tetragonal site model and (b) its associated rotational processes proposed by Fitzsimmons and Hume [22,23].

would amount to $R \ln 6$ ($= 14.90$ J K^{-1} mol^{-1}) because the molecular axis of the cation can orient in x, y, z-directions and in addition to this one can distinguish the head of the cation from its tail. The present calorimetric value of 14.55 J K^{-1} mol^{-1} supports their reorientational model. The reason why the reorientational motion of the cation is excited not by a single phase transition but by multi-transitions (T_{C3}, T_{C2} and T_{C1}) may be associated with the fact that the six orientations are energetically non-equivalent. According to ^{57}Fe Mössbauer spectroscopy [22,23], the molecular orientation in the z-direction is 2.0 kJ mol^{-1} lower than those in the x- and y-directions, and furthermore the activation energy hindering a jump between two orientations is $E_{xy} = 10$ kJ mol^{-1} and $E_{zx} = E_{zy} = 20$ kJ mol^{-1}. Therefore, multi-phase transitions found in the present calorimetric study seem to correspond to a stepped excitation of the jump reorientations. It should, however, be remarked here that the entropy of $R \ln 6$ has been derived by assuming an axial symmetry of C_∞ for the cation even on the low-temperature side of "the higher-temperature phase transition", i.e., phase IV in the present case. In other words, the $[Fe(C_5H_5)(C_6H_6)]^+$ cation has been assumed to make a free rotation around its molecular axis in phase IV. If the cation is in a fixed orientation without rotating about its axis in phase IV, one can expect a much larger transition entropy than $R \ln 6$: the degree of excess entropy depends on the number of available energetically-equal orientations about the molecular axis in phase I.

In relation to this unsettled problem whether or not the cation is still reorienting about its molecular axis in phase IV, the existence of the lower-temperature phase transition at T_{C4} seems to be of interest. Although this phase transition is essentially of first order, it bears the nature of a higher-order phase transition in the sense that the excess heat capacity, ΔC_p, evolves over a wide temperature region below T_{C4}. The transition entropy, though somewhat diminished by two glass transition phenomena, is still as large as 8.01 J K^{-1} mol^{-1}. For the origin responsible for this phase transition, we shall discuss three possibilities: (i) a pure crystallographic change, (ii) onset of reorientational motion of the cation about its molecular axis and (iii) an order–disorder phenomenon of the PF_6^- anion.

Firstly, we can discard the first possibility of a crystallographic change for the following reason. Owing to different phonon spectra, a change in crystal structure generally brings about a discontinuity at the transition temperature between two normal heat-capacity curves extrapolated from high- and low-temperature phases, but this is not the case here. Another unfavorable factor which goes against this possibility is the presence of a glass transition phenomenon on the low-temperature side of this phase transition point. Molecular modes quenched during a glass transition in a crystalline state (the so-called glassy crystal) are usually in the conformation or configuration of molecules [33,34]. Moreover, the transition entropy seems to be too large to account for a structural change at such a low temperature.

Secondly, the reorientational order–disorder of the $[Fe(C_5H_5)(C_6H_6)]^+$ cation around its molecular axis seems to be a possible mechanism to account for this phase transition. Unfortunately, however, we cannot conclude this mechanism solely from the present calorimetric study. To confirm whether or not this is the case, ^1H or ^2H NMR techniques must be used to provide us with definitive evidence.

Finally, the third possibility of an order–disorder phenomenon of the PF_6^- anion is also a plausible candidate for the origin of the phase transition. As will be described below, the analogous salt, $[Fe(C_5H_5)_2]^+(PF_6)^-$, also shows a phase transition at 210 K with a similar magnitude transition entropy (9.54 J K^{-1} mol^{-1}). The only difference between these two substances is their cations: one is a metallocene having five- and six-membered rings while the other is a metallocene with two five-membered rings. Octahedral anions such as the present PF_6^- are most likely to display orientational disorder [1]. For example, Staveley et al. [35] have reported phase transitions attributable to an order–disorder change in some simple salts of hexafluorophosphates: $T_C = 273.87$ K and $\Delta_{trs}S = 28.74$ J K^{-1} mol^{-1} for KPF_6; $T_C = 207$ K and $\Delta_{trs}S = 10.13$ J K^{-1} mol^{-1} for $RbPF_6$; $T_C = 191.8/131.3$ K and $\Delta_{trs}S = 9.33/10.38$ J K^{-1} mol^{-1} for NH_4PF_6. Since we are only concerned with the transition entropy, the value determined for the present salt (8.01 J K^{-1} mol^{-1}) is comparable with those for $RbPF_6$ and NH_4PF_6. ^{19}F NMR may serve as a powerful experimental method to give a clue to the elucidation of the nature of the PF_6^- anions across the present phase transition.

$[Fe(C_5H_5)_2]^+(PF_6)^-$

The $[Fe(C_5H_5)_2]^+$ cation of the present salt is simpler than $[Fe(C_5H_5)(C_6H_6)]^+$ in the sense that its molecular orientation is identical whether interchanged up or down, whereas the head and tail of the $[Fe(C_5H_5)(C_6H_6)]^+$ cation can be discriminated from each other. Therefore, the reorientational entropy of a phase transition for $[Fe(C_5H_5)_2]^+(PF_6)^-$, if any, corresponding to the higher-temperature phase transition of $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$, would be expected to be $R \ln 3$ (= 9.13 J K^{-1} mol^{-1}) rather than $R \ln 6$ (= 14.90 J K^{-1} mol^{-1}).

Figure 6 illustrates the results of heat capacity measurements. As has been expected, this compound exhibited the phase transition at 346.94 K (denoted as T_{C1}). The transition temperature was 25 K higher than that found for $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$. In addition to this phase transition, low-temperature phase transitions were also observed at 213.05 and 210.95 K (T_{C2} and T_{C3}, respectively). Although the gross aspect of the present heat capacity curve bears some resemblance to that of $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$, one notices a few differences between the two: one is the absence of the glass transition phenomenon in the lowest-temperature phase and the other is a

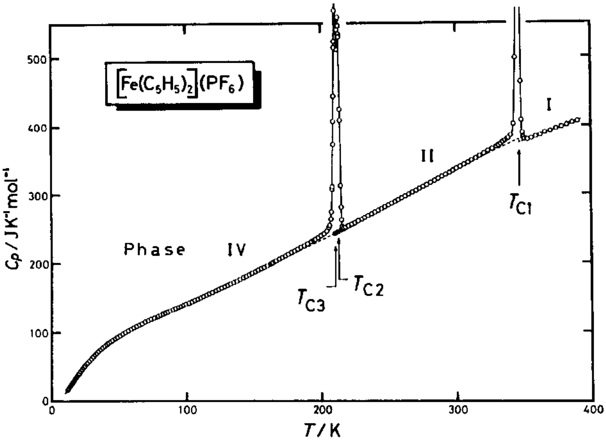

Fig. 6. Molar heat capacities of $[Fe(C_5H_5)_2]^+(PF_6)^-$ between 12 and 393 K. The solid circles indicate the heat capacities of the undercooled high-temperature phase. The broken curve indicates the normal heat capacity.

lack of the subsidiary heat capacity peaks corresponding to the "pre-transition" of the highest-temperature phase transition for $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$.

As shown in Table 3, the entropy arising from the higher-temperature phase transition at T_{C1} was as large as 13.99 J K^{-1} mol^{-1}, which is comparable with the value of 14.55 J K^{-1} mol^{-1} found for $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$. This unexpected fact has constrained us to choose an alternative picture for the transition mechanism of $[Fe(C_5H_5)_2]^+(PF_6)^-$. In passing it should be remarked here that the highest-temperature phase of $[Fe(C_5H_5)_2]^+(PF_6)^-$ (phase I) also belongs to a cubic system, which we confirmed optically: as in the case of $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$ crystal, we observed that the polarizing colors disappear completely at T_{C1} under a polarizing microscope. A possible reorientational model in phase I, which fulfills a cubic symmetry, is that the molecular axis of $[Fe(C_5H_5)_2]^+$ cation reorients among six face-diagonal directions of a cubic lattice formed by eight PF_6^- anions. If this is the case, the transition entropy due to such a reorientational mechanism becomes $R \ln 6$ ($= 14.90$ J K^{-1} mol^{-1}) and the observed

TABLE 3

The enthalpy and entropy arising from the phase transitions of $[Fe(C_5H_5)_2]^+(PF_6)^-$

Transition	T_C (K)	$\Delta_{trs}H$ (kJ mol^{-1})	$\Delta_{trs}S$ (J K^{-1} mol^{-1})
Phase IV → III	T_{C3}: 210.95	1.95	9.54
III → II	T_{C2}: 213.05		
II → I	T_{C1}: 346.94	4.84	13.99

entropy (13.99 J K^{-1} mol^{-1}) can be well accounted for by this model, though somewhat ad hoc.

On the other hand, the entropy gain (9.54 J K^{-1} mol^{-1}) concerning the lower-temperature phase transition was also comparable with the value of 8.01 J K^{-1} mol^{-1} found for $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$. The transition mechanism may, therefore, be considered to be analogous to that of $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$. A possible candidate responsible for the phase transition is orientational order–disorder of the PF_6^- anion. In this case, the number of energetically-equivalent orientations of the PF_6^- anion above the low-temperature phase-transition point might be three because the observed transition entropy can be well approximated by R ln 3 (= 9.13 J K^{-1} mol^{-1}). Detailed experimental results and discussion will be described elsewhere [36].

CONCLUDING REMARKS

Heat capacity measurements have been used to demonstrate the presence of several phase transitions in three organometallic compounds: $Fe(C_5D_5)_2 \cdot 3(NH_2)_2CS$, $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$ and $[Fe(C_5H_5)_2]^+(PF_6)^-$. Among the many phase transitions observed for these three compounds, the dominant phase transition in each compound was concluded to arise from a reorientational order–disorder mechanism of the molecular axis of $Fe(C_5D_5)_2$, $[Fe(C_5H_5)(C_6H_6)]^+$ or $[Fe(C_5H_5)_2]^+$ in the clathrate-cavity or in the pseudo-cavity formed by eight PF_6^- anions. The present conclusion, derived from the entropic viewpoint, has clearly proved the predictions of the possible existence of phase transitions given by ^{57}Fe Mössbauer spectroscopic measurements [20,22,23].

For the new low-temperature phase transitions found for $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$ and $[Fe(C_5H_5)_2]^+(PF_6)^-$, we proposed a transition mechanism in which the PF_6^- anion undergoes a reorientational order–disorder change. In confirmation of this possibility, ^{19}F NMR seems to be a decisive experimental method along with X-ray structural work.

One of the interesting and still unsettled problems is a question about whether or not $Fe(C_5D_5)_2$ and the cations, $[Fe(C_5H_5)(C_6H_6)]^+$ and $[Fe(C_5H_5)_2]^+$, are still reorienting around their molecular axes in the lowest-temperature phase. In the case of ferrocene-h_{10}–thiourea clathrate compound, ^{1}H NMR has shown a very small value of 1.0 G^2 for the second moment in the lowest-temperature phase, which is slightly larger than 0.6 G^2 expected for free-rotation of the cyclopentadienyl rings around the molecular axis of ferrocene, but extremely small compared with the rigid value of 2.4 G^2 [30]. This fact indicates ongoing reorientational motion of the cyclopentadienyl rings around the molecular axis of ferrocene. A similar situation can easily be expected for the three compounds studied here. If the reorientational motion of the five- or six-membered rings around the molecular axis of "ferrocene" were ceased cooperatively, a phase transition would be observed below 13 K. Heat capacity measurements in this temperature region are thus being planned.

Along with this problem, the low-temperature heat-capacity of $[Fe(C_5H_5)_2]^+(PF_6)^-$ seems to be of great interest from the viewpoint of magnetism. Since the ground electronic state of $[Fe(C_5H_5)_2]^+$ cation is $^2E_{2g}(a_{1g})^2(e_{2g})^3$ [37] and the compound remains paramagnetic down to 4.2 K [25,38,39], a heat capacity anomaly associated with the magnetic ordering would be expected to occur below 4.2 K.

REFERENCES

1 N.G. Parsonage and L.A.K. Staveley, Disorder in Crystals, Clarendon Press, Oxford, 1978.
2 E.O. Fischer and W. Pfab, Z. Naturforsch., Teil B, 7 (1952) 377.
3 G. Wilkinson, M. Rosenblum, M.C. Whiting and R.B. Woodward, J. Am. Chem. Soc., 74 (1952) 2125.
4 J.W. Edwards, G.L. Kington and R. Mason, Trans. Faraday Soc., 56 (1960) 660.
5 J.W. Edwards and G.L. Kington, Trans. Faraday Soc., 58 (1962) 1334.
6 J.D. Dunitz, L.E. Orgel and A. Rich, Acta Crystallogr., 9 (1956) 373.
7 G. Calvarin and J.F. Berar, J. Appl. Crystallogr., 8 (1975) 380.
8 P. Seiler and J.D. Dunitz, Acta Crystallogr., Sect. B, 35 (1979) 1068.
9 F. Takusagawa and T.F. Koetzle, Acta Crystallogr., Sect. B, 35 (1979) 1074.
10 P. Seiler and J.D. Dunitz, Acta Crystallogr., Sect. B, 35 (1979) 2020.
11 K. Ogasahara, M. Sorai and H. Suga, Chem. Phys. Lett., 68 (1979) 457.
12 K. Ogasahara, M. Sorai and H. Suga, Mol. Cryst. Liq. Cryst., 71 (1981) 189.
13 J.F. Berar, G. Calvarin, D. Weigel, K. Chhor and C. Pommier, J. Chem. Phys., 73 (1980) 438.
14 P. Seiler and J.D. Dunitz, Acta Crystallogr., Sect. B, 38 (1982) 1741.
15 J.S. Bodenheimer and W. Low, Phys. Lett. A, 36 (1971) 253.
16 M. Naruse, M. Sorai and M. Sakiyama, Mol. Cryst. Liq. Cryst., 101 (1983) 219.
17 Y. Shiomi and M. Sorai, Chem. Phys. Lett., 95 (1983) 167.
18 M. Sorai and Y. Shiomi, Mol. Cryst. Liq. Cryst., 107 (1984) 271.
19 R. Clement, R. Claude and C. Mazieres, J. Chem. Soc., Chem. Commun., (1974) 654.
20 T.C. Gibb, J. Phys. C: Solid State Phys., 9 (1976) 2627.
21 M. Sorai, K. Ogasahara and H. Suga, Mol. Cryst. Liq. Cryst., 73 (1981) 231.
22 B.W. Fitzsimmons, J. Phys. (Paris), 41 (1980) C1-33.
23 B.W. Fitzsimmons and A.R. Hume, J. Chem. Soc., Dalton Trans., (1980) 180.
24 R.B. King, Organometall. Synth., 1 (1965) 138.
25 D.N. Hendrickson, Y.S. Sohn and H.B. Gray, Inorg. Chem., 10 (1971) 1559.
26 M. Yoshikawa, M. Sorai, H. Suga and S. Seki, J. Phys. Chem. Solids, 44 (1983) 311.
27 K. Tsuji, M. Sorai, H. Suga and S. Seki, Mol. Cryst. Liq. Cryst., 55 (1979) 71.
28 M. Sorai and S. Seki, J. Phys. Soc. Jpn., 32 (1972) 382.
29 E. Hough and D.G. Nicholson, J. Chem. Soc., Dalton Trans., (1978) 15.
30 R. Clement, M. Gourdji and L. Guibe, Chem. Phys. Lett., 72 (1980) 466.
31 Y. Shiomi and M. Sorai, Comparison of heat capacity of $Fe(C_5D_5)_2 \cdot 3(NH_2)_2CS$ with the $Fe(C_5H_5)_2$ analog, manuscript in preparation.

32 Y. Shiomi and M. Sorai, Glass transition phenomenon in $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$, manuscript in preparation.

33 H. Suga and S. Seki, J. Non-Cryst. Solids, 16 (1974) 171.

34 H. Suga and S. Seki, Faraday Discuss., 69 (1980) 221.

35 L.A.K. Staveley, N.R. Grey and M.J. Layzell, Z. Naturforsch., Teil A, 18 (1963) 148.

36 Y. Shiomi and M. Sorai, Heat capacity measurements of $[Fe(C_5H_5)_2]^+(PF_6)^-$ and comparison of the phase transitions with those of $[Fe(C_5H_5)(C_6H_6)]^+(PF_6)^-$, manuscript in preparation.

37 R. Prins and F.J. Reinders, J. Am. Chem. Soc., 91 (1969) 4929.

38 Y.S. Sohn, D.N. Hendrickson and H.B. Gray, J. Am. Chem. Soc., 92 (1970) 3233.

39 D.N. Hendrickson, Y.S. Sohn, D.M. Duggan and H.B. Gray, J. Chem. Phys., 58 (1973) 4666.