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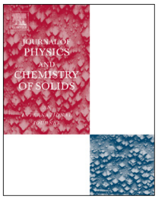

Heat capacity of paramagnetic nickelocene: Comparison with diamagnetic ferrocene[☆]

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ABSTRACT

Nickelocene [bis(η^5-cyclopentadienyl)nickel: $Ni(C_5H_5)_2$, electron spin $S=1$, the ground state configuration $^3A_{2g}$] is paramagnetic and belongs to a typical molecule-based magnet. Heat capacities of nickelocene have been measured at temperatures in the 3–320 K range by adiabatic calorimetry. By comparing with those of diamagnetic ferrocene crystal, a small heat capacity peak centered at around 15 K and a sluggish hump centered at around 135 K were successfully separated. The low-temperature peak at 15 K caused by the spin is well reproduced by the Schottky anomaly due to the uniaxial zero-field splitting of the spin $S=1$ with the uniaxial zero-field splitting parameter $D/k=45$ K (k: the Boltzmann constant). The magnetic entropy 9.7 J K^{-1} mol^{-1} is substantially the same as the contribution from the spin-manifold $R \ln 3 = 9.13$ J K^{-1} mol^{-1} (R: the gas constant). The sluggish hump centered at around 135 K arises from rotational disordering of the cyclopentadienyl rings of nickelocene molecule. The enthalpy and entropy gains due to this anomaly are 890 J mol^{-1} and 6.9 J K^{-1} mol^{-1}, respectively. As the hump spreads over a wide temperature region, separation of the hump from the observed heat capacity curve involves a little bit ambiguity. Therefore, these values should be regarded as being reasonable but tentative. The present entropy gain is comparable with 5.5 J K^{-1} mol^{-1} for the sharp phase transition at 163.9 K of ferrocene crystal. This fact implies that although the disordering of the rings likewise takes place in both nickelocene and ferrocene, it proceeds gradually in nickelocene and by way of a cooperative phase transition in ferrocene. A reason for this originates in loose molecular packing in nickelocene crystal. Molar heat capacity and the standard molar entropy of nickelocene are larger than those of ferrocene beyond the mass effect over the whole temperature region investigated. This fact provides with definite evidences for the loose molecular packing in nickelocene crystal.

1. Introduction

Along with ferrocene, nickelocene [bis(η^5-cyclopentadienyl) nickel: $Ni(C_5H_5)_2$] is a representative key-substance of sandwich-type organometallic compounds. Although the molecular and crystal structures of nickelocene [1] are identical with those of ferrocene [2] at room temperature, thermal behaviors are quite different. As to ferrocene, Edwards et al. [3,4] discovered a λ-type phase transition at 163.9 K due to orientational disordering of the cyclopentadienyl C_5H_5-rings, which occurs between triclinic low-temperature (LT) phase and monoclinic high-temperature (HT) phase. However, X-ray diffraction [5–9], neutron scattering [10], and Mössbauer spectroscopy [11] reported thereafter revealed that the mechanism of the phase transition is not so simple. On the other hand, we found a stable LT-phase of ferrocene which can persist stably below 242 K and is transformed to the monoclinic HT-phase at this temperature on heating [12,13]. This fact revealed that the well-known λ-type phase transition at 163.9 K is a phenomenon occurring between the thermodynamically metastable triclinic LT-phase and the undercooled monoclinic HT-phase. The crystal structure of the stable LT-phase was found to be orthorhombic with space group *Pnma* (molecule per unit cell: $Z=4$) [14,15]. Moreover Bodenheimer and Low [16] discovered that ferrocene crystal disintegrates violently in the triclinic LT-phase on cooling. We accurately determined the heat evolved when ferrocene crystals disintegrate and found that quite interestingly it is larger than the enthalpy gain at the λ-type phase transition [12,13,17]. In contrast, nickelocene crystal exhibits neither such phase transitions nor crystal disintegration.

A clue to understand the different phase behaviors and the crystal disintegration may surely be hidden in their thermodynamic quantities. To this end, accurate heat capacity data of both metallocenes from low temperature are necessary. As to ferrocene, heat capacities have been reported by Edwards et al. [3,4] and Ogasahara et al.

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[12,13]. These two sets of data agree well. As to nickelocene, Azokpota et al. [18] measured its heat capacities in the temperature range 130 – 300 K by differential scanning calorimetry (DSC) and Rabinovich et al. [19] reported the heat capacities in the 4.5 – 305 K temperature range measured by adiabatic calorimetry. However, the heat capacities reported by two research groups are largely different. We report in this paper heat capacity measurements for nickelocene in the 3 – 320 K range by adiabatic calorimetry and compare the results with those of ferrocene [12,13].

Another difference between nickelocene and ferrocene is that although ferrocene is diamagnetic, nickelocene is a paramagnet characterized by electron spin $S = 1$ with the ground state configuration $^3A_{2g}$ [20–24] and belongs to a typical molecule-based magnet [25]. In the last two decades, various kinds of molecule-based magnets have been synthesized, and their chemical and physical properties have been elucidated from microscopic and macroscopic standpoints by use of various experimental methods. Among them, thermodynamic methods are unique in the sense that the energetic and entropic aspects inherent in materials can be directly observed. As nickelocene is a typical molecule-based magnet having simple molecular structure, calorimetric investigation for this material provides useful information to the general understanding of the molecule-based magnets.

2. Experimental

2.1. Preparation of sample

Commercially available nickelocene (Tokyo Kasei Kogyo Co., Ltd.) was purified twice by sublimation in a vacuum at 45 – 55 °C. Well-developed dark green crystals were obtained by slow sublimation. In order to avoid degradation of the purified nickelocene crystals by air and moisture, the sample was treated in an atmosphere of dry argon. Elemental analysis yielded the following mass percentages. Calcd. for $C_{10}H_{10}Ni$: C, 63.59; H, 5.34; Ni, 31.07%. Found: C, 63.56; H, 5.43%.

2.2. Physical methods

Prior to heat capacity measurements, thermal behavior of nickelocene crystal was preliminarily examined by use of home-built differential thermal analysis (DTA) apparatus in the 80 – 450 K temperature range.

Heat capacity measurements in the 12 – 320 K temperature range were performed by use of an adiabatic calorimeter [26]. Mass of the specimen loaded in the calorimeter cell was 13.8291 g (0.0732166 mol) and the density of crystal assumed for buoyancy correction was 1.33 g cm^{-3} [1]. To aid the heat transfer inside the calorimeter-cell, a small amount of helium gas at 60 kPa was sealed in the cell. Heat capacities in the 1 – 25 K temperature range were measured by a very-low temperature calorimeter with a (^{3}He + ^{4}He) dilution refrigerator [27]. Mass of the specimen was 8.4996 g (0.045000 mol). A small amount of helium gas at 8 kPa was sealed in the cell. The heat capacity of the sealed helium gas estimated as the ideal gas was subtracted from the observed value.

It should be noted that the amounts of specimen used for the present works are surprisingly large in comparison to present-day calorimetry because the measurements were made a quarter of a century ago.

3. Results

Cooling DTA runs for nickelocene were performed with different rates but neither exothermic peak due to a phase transition nor a peak due to crystal disintegration was observed. This fact contrastively differs from the case of ferrocene, which shows a phase transition and dramatic disintegration of crystal on cooling [12,13,16,17]. Contrary to ferrocene [3,4,12,13], no endothermic peak due to a crystal-to-crystal phase transition was observed on heating from 80 K to room temperature. Nickelocene crystal decomposed with heat evolution just above its melting at 445 K.

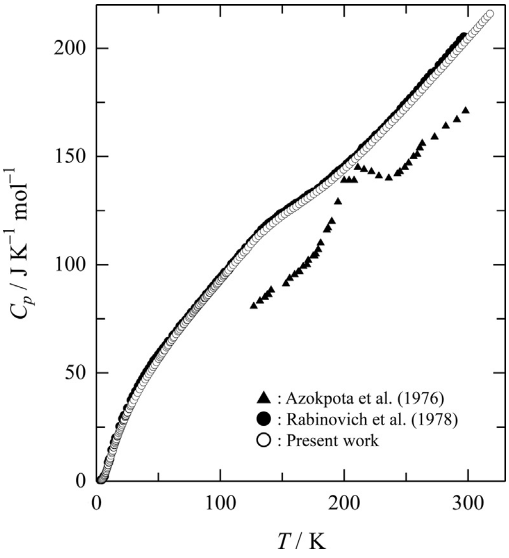

Fig. 1. Molar heat capacities of nickelocene. ▲: C_p values derived from DSC by Azokpota et al. [18]. ●: C_p values determined with adiabatic calorimetry by Rabinovich et al. [19]. ○: present C_p values determined with adiabatic calorimetry.

Heat capacity measurements by use of the adiabatic calorimeter [26] were performed in five series at temperatures in the 12 – 320 K range. The results were evaluated in terms of C_p, the molar heat capacity under constant pressure, and listed in Table A1 (Electronic Annex of this paper). On the other hand, heat capacities were determined in two series at temperatures in the 1 – 25 K range by use of the very-low temperature calorimeter with a (^{3}He + ^{4}He) dilution refrigerator [27]. However, as the data below 3 K involved undesirable error due to desorption of the heat-exchange helium gas adsorbed on the surfaces of nickelocene crystals, those data were deleted. The heat capacity data in the 3 – 25 K range are listed in Table A2 (Electronic Annex of this paper). As plotted in Fig. 1, the present heat capacities agree well with those determined with adiabatic calorimetry by Rabinovich et al. [19]. The heat capacity difference is less than 1.5 per cent above 70 K, while it increases with lowering temperature: 3.8 per cent at 50 K, 6.2 per cent at 20 K, and 8.1 per cent at 10 K. On the other hand, the heat capacities determined with DSC by Azokpota et al. [18] are considerably lower than those determined with adiabatic calorimetry. As presumed by Rabinovich et al. [19], this might possibly be due to a less pure sample used by Azokpota et al. [18].

4. Discussion

Heat capacities of nickelocene are compared to those of ferrocene [12,13] in Fig. 2. Although the relative molecular mass of nickelocene ($M_r = 188.867$) is a little bit heavier than ferrocene ($M_r = 186.019$), the heat capacities of nickelocene are much larger than those of ferrocene, beyond the mass effect, over the whole temperature region investigated. The crystal system of nickelocene is monoclinic and the space group is $P2_1/a$ with $Z = 2$ [1,28], which is identical with that of ferrocene in the room-temperature phase [2]. By taking this fact into account, the enhanced heat capacity of