Precise measurements of diamagnetic susceptibility of benzophenone and paraffin by using a magnetic levitation technique

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Abstract. Measurements for temperature dependence of diamagnetic susceptibility were performed under the magnetic levitation condition. The magnetic susceptibility of a single crystal of benzophenone showed monotonous decrease toward to the melting point with increasing temperature. The minimum change of the susceptibility was detected by $1.4 \times 10^{-12}$ m$^3$/kg. On the contrary, slight increase was observed below the melting point in the case of paraffin. The susceptibility of a paraffin melt was found to be smaller than that of the solid state. It was demonstrated that the magnetic levitation enables sensitive and contactless measurements of the diamagnetic susceptibility across the melting point.

1. Introduction
Diamagnetic materials in a magnetic field gradient receive a repulsive force. When the upward magnetic force counterbalances with the downward gravitational force, the materials can be levitated [1]. In this magnetic levitation state, such a counterbalance holds for each molecule or atom constituting the materials, hence the magnetic levitation is considered to be a quasi-microgravity condition. The magnetic levitation enables containerless melting of materials, which is a novel technique for materials synthesis using high magnetic fields [2-4]. For melting and solidifying a material without any contacts through the whole process, it is very important to know the temperature dependence of diamagnetic susceptibility of the material. It is generally known that the temperature dependence of diamagnetic susceptibility is very small or negligible. A slight change in the susceptibility, however, affects the sample position in the magnetic levitation. Actually, it was observed that a sample moves slightly upward or downward during heating process in our previous experiments. This shows that the magnetic levitation condition is quite sensitive to the magnetic susceptibility change. The magnetic levitation enables to measure the temperature dependence of diamagnetic susceptibility precisely.

For a diamagnetic material placed in the vertical bore of a solenoidal electromagnet, the magnetic force per unit mass of the material in the vertical direction $F_{\text{mag}}$ is given by

$$F_{\text{mag}} = \frac{1}{\mu_0} \chi g B (\partial B/\partial z),$$

(1)
where $\chi_b$ is the magnetic susceptibility per unit mass, $\mu_0$ the vacuum permeability and $B$ the magnetic flux density at distance $z$ from the magnet center. When $F_{\text{mag}}$ acts upward and balances with the downward force due to the gravity $g$ i.e. $F_{\text{mag}} = g$, the material levitates; that is the magnetic levitation condition. In such a condition, the magnetic susceptibility of the material is evaluated as,

$$\chi_b = g / \mu_0 B (\partial B / \partial z).$$

The magnetic force field $B (\partial B / \partial z)$ can be obtained from calculations of the field distribution of a magnet in which the sample levitates.

Measurements of diamagnetic susceptibility have been performed by using the magnetic levitation technique by Tanimoto et al [5]. They determined the susceptibilities of some plastics from $B (\partial B / \partial z)$ at different levitating positions depending on the susceptibilities at room temperature.

A sample position will change when its susceptibility decreases or increases in a heating process. When the change of the susceptibility is large, a sample will fly away or fall down by losing its stable position. In order to perform wide range measurements of the susceptibility change, it is better to control a sample position when a sample moves. Thus we demonstrate sensitive measurements of diamagnetic susceptibility of a levitating sample with adjusting the magnetic field to keep a sample in a given position.

2. Experimental

Benzophenone crystal (molecular formula: $(C_6H_5)_2CO$) belongs to the orthorhombic symmetry and the unit cell dimensions are $a = 10.26$, $b = 12.09$, $c = 7.88$ Å [6]. The magnetic susceptibilities of the crystal have been reported to be $\chi_a = -6.07 \times 10^{-9}$, $\chi_b = -6.11 \times 10^{-9}$ and $\chi_c = -10.3 \times 10^{-9}$ m$^3$/kg [7]. A single crystal of benzophenone (Wako Pure Chemical Industries, Ltd., 98.0%) with the nominal melting point of 48-50°C was employed for this work and its size was about $1.5 \times 1.5 \times 3$ mm$^3$.

Paraffin $(C_{n}H_{2n+2})$ is composed of single C–C bonds combining like a chain. A single C–C bond has a diamagnetic anisotropy of $\Delta \chi = \chi_\parallel - \chi_\perp = -16 \times 10^{-12}$ m$^3$/mol [8], where $\chi_\parallel$ is the magnetic susceptibility parallel to the bond and $\chi_\perp$ perpendicular to the bond. Paraffin with the melting point 48-56 and 56-58°C (Wako Pure Chemical Industries, Ltd.) were used for measurements. Samples for levitation experiment were cut from purchased bulk into about $4 \times 4 \times 4$ mm$^3$ pieces.

In order to achieve the magnetic levitation of benzophenone or paraffin, a hybrid magnet (28T-HM) was used, which consists of an inner water-cooled resistive magnet and an outer superconducting magnet. This magnet can generate up to $-3200$ T$^2$/m of $B (\partial B / \partial z)$ at the central field of 27 T. Temperature was controlled from 20 to 60°C by using a water circulating thermostatic bath set in a 52 mm room temperature bore of the magnet as illustrated in figure 1. Temperature in the bath was measured by a copper-constantan thermocouple. A sample was put in a sample cell with nitrogen gas and the cell was shield with Sealon film (Fuji Photo Film Co., Ltd.). Buoyancy caused by paramagnetic oxygen gas in the air, so called the magneto-Archimedes effect, did not affect the levitation condition in this case. The behavior of a levitating sample was observed by a CCD camera through a prism and images were recorded on a DVD recorder.

The measurement procedure was as follows. As a first step, a sample was levitated at a certain position by adjusting the magnetic field. Then temperature was raised to the next measurement temperature at a rate of less than $1\degree$ C/min. If the sample moved upward or downward during the process, the magnetic field was adjusted in order that the sample may move back to the initial position. Figure 2 shows snap shots of a benzophenone during the process to keep a levitating position mentioned above. The value of $B (\partial B / \partial z)$ to levitate the sample at the temperature was determined after the sample kept the position stably.

3. Results and discussion
Figure 1. Schematic illustration of an experimental setup for magnetic susceptibility measurements using the magnetic levitation technique.

Figure 2. A position change of a levitating benzophenone during a heating process. The temperature and the magnetic field are: (a) 20°C, 22.676 T, (b) 22°C, 22.676 T and (c) 22°C, 22.675 T, respectively. Δz in this figure is about 0.15 mm.

A single crystal of benzophenone at 20°C was levitated at the central field of 22.676 T, which corresponded to $B(\partial B/\partial z) = -2014.0 \ T^2/m$. The temperature dependence of the magnetic susceptibility per unit mass of benzophenone is shown in figure 3. The susceptibility decreased monotonously as increasing temperature, and decreased rapidly a few degrees below the melting point of 48°C. In the case of benzophenone, a control of the levitating position could not continue and the sample fell down because a change of the susceptibility was very large over 41°C. This temperature dependence behavior is considered as follows. At first a single crystal of benzophenone levitated as the $a$-axis is parallel to the magnetic field direction to minimize the magnetic energy, because the susceptibility along the $a$-axis is larger (smaller in the absolute value) than others. Then thermal vibration of molecules became larger with increasing temperature, and the susceptibility became smaller toward the value of the liquid state. Assuming that the value of the magnetic susceptibility in the liquid state of benzophenone is the average of values along each axis, it is to be $-7.49 \times 10^{-9} \ m^3/kg$.

The change of the susceptibility could be detected by $1.4 \times 10^{-12} \ m^3/kg$ as the minimum value between at 20 and 24°C in this work, it was 0.02% of the value at 20°C of $-6.1189 \times 10^{-9} \ m^3/kg$. This indicates that the magnetic levitation is one of useful methods for sensitive measurements of the diamagnetic susceptibility change.

Paraffins were levitated at $z = 98.9 \ mm$ at the central field of 18.629 T (m.p. = 56-58°C) and 18.554 T (m.p. = 48-50°C) at 20°C. Figure 4 shows the temperature dependences of the magnetic susceptibility per unit mass of paraffins. In the case of paraffins, both samples were heated to melt.
Figure 3. Temperature dependence of the magnetic susceptibility per unit mass of benzophenone.

state just above the melting point continuously. Snap shots of paraffin (m.p. = 48-50°C) in during heating process are shown in figure 5. Temperature dependence behavior of both samples were similar qualitatively and different from the case of benzophenone. The susceptibility increased with increasing temperature below the melting point and then decreased in the melt state. Paraffins used in this work were mixture of n-alkanes, which undergo solid-solid phase transitions just below the melting point and transition temperatures depend on the carbon number [9]. Slight increase observed in the

Figure 4. Temperature dependence of magnetic susceptibility per unit mass of paraffin (m.p. = 48-50°C).

Figure 5. Snap shots of a levitating paraffin (m.p. = 48-50°C) in a heating process. Temperatures are; (a) 20°C, (b) 30°C, (c) 42°C, (d) 46°C and (e) 52°C, respectively.
temperature dependence of the magnetic susceptibility was possibly caused by this phase transitions. Increasing in the susceptibility means that the magnetic orientation may occur accompanied with the phase transitions. To confirm this, it is necessary to measure the temperature dependence of the susceptibility of a monodisperse \( n \)-alkane.

Magnetic susceptibility measurements by using magnetic levitation technique have advantages compared to conventional methods as follows. (1) Large size sample is not necessary for measurements. A small sample less than 1 mm in length is enough to be measured if a sample is observable on a TV monitor. (2) No sample holder is needed to support a sample in measurements. In most of cases in magnetization measurements, magnetic moment of a sample holder is to be a background to the signal of a sample. (3) In heating process, the magnetic susceptibility can be measured across the melting point continuously with \textit{in-situ} observations as shown in figure 5. In order to obtain higher accuracy in the absolute value, the more exact value of \( B(\partial B/\partial z) \) at a sample levitating position is required. However, relative change in the temperature dependence of the susceptibility can be detected sensitively by using this method as reported in this paper.

4. Conclusion
Diamagnetic susceptibility measurements of benzophenone and paraffin were demonstrated by using a magnetic levitation technique. Temperature dependences of the susceptibility were obtained for both samples. The minimum change in the susceptibility could be detected by \( 1.4 \times 10^{-12} \) m\(^3\)/kg in the heating process of benzophenone. From the results, it was found that the magnetic levitation is one of the most useful methods for sensitive measurements of the diamagnetic materials. By using this method, temperature dependence of the susceptibility across the melting point can be obtained without any contacts.

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