THERMOPHYSICAL PROPERTIES OF MOLTEN GERMANIUM
MEASURED BY THE HIGH TEMPERATURE ELECTROSTATIC LEVITATOR

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ABSTRACT

Thermophysical properties of molten germanium such as the density, the thermal expansion coefficient, the hemispherical total emissivity, the constant pressure specific heat capacity, the surface tension, and the electrical resistivity have been measured using the High Temperature Electrostatic Levitator at JPL. The measured liquid density can be expressed by 
\[ \rho_{\text{liq.}} = 5.67 \times 10^3 - 0.542 (T - T_m) \quad \text{Kg m}^{-3} \quad (1150 \sim 1400 \text{ K}) \] with \( T_m = 1211.3 \text{ K} \), the volume expansion coefficient by \( \alpha = 0.9656 \times 10^{-4} \text{ K}^{-1} \), and the hemispherical total emissivity at the melting temperature by \( \varepsilon_{T,\text{liq}(T_m)} = 0.17 \). Assuming constant \( \varepsilon_{T,\text{liq}(T)} = 0.17 \) in the liquid range which have been investigated, the constant pressure specific heat was evaluated as a function of temperature (see Fig. 5 in the text). The surface tension over the same temperature range can be expressed by \( \sigma(T) = 583 - 0.08 (T - T_m) \quad \text{mN m}^{-1} \) and the temperature dependence of electrical resistivity of molten germanium, when \( r_{\text{liq}}(T_m) = 60 \quad \mu\Omega\text{cm} \) is used as a reference point, can be expressed by \( r_{e,\text{liq}(T)} = 60 +1.18 \times 10^{-2} (T - 1211.3) \quad \mu\Omega\cdot\text{cm} \). The thermal conductivity which is determined by the resistivity data according to the Wiedemann-Franz-Lorenz law is given by \( \kappa_{\text{liq}(T)} = 49.43 + 2.90 \times 10^{-2} (T - T_m) \quad \text{W m}^{-1} \text{K}^{-1} \).

KEY WORDS: Electrostatic levitation; molten germanium; density; hemispherical total emissivity; specific heat; surface tension; electrical resistivity; thermal conductivity.
1. INTRODUCTION

Thermophysical properties of molten semiconductors are needed in understanding the liquid structures and the solidification process in general, and for the numerical modeling of crystal growth processes in particular. Although solid germanium has been rather extensively investigated, properties of molten germanium are rather scarce. Even then, of they exist, there are substantial differences among them.

In this paper, we revisit the molten germanium, this time with various non-contact methods, and report its properties such as the density, the volume expansion coefficient, the hemispherical total emissivity, the specific heat, the surface tension, and the temperature dependence of electrical resistivity. These properties have been measured using the High Temperature Electrostatic Levitator (HTESL) which isolated the samples from container walls during entire experiments in a high vacuum condition. Under such condition, the purity of samples could be maintained, highly undercooled liquid states are expected, and their properties can be measured using appropriate non-contact diagnostic techniques which have been developed for the HTESL.

The HTESL[1] at JPL can levitate conducting as well as semiconducting materials. Some of the characteristics of HTESL which made the present work possible are: (i) it can levitate a pure germanium sample one at a time, melt it while in levitation, and can reach an undercooled state when it is cooled, (ii) the sample heating and the levitation do not interfere each other so that the sample can be cooled in a purely radiative manner when the heating source was either turned off or blocked. This allowed description of the whole cooling process by a well defined heat transfer equation, allowing accurate measurement of \( \frac{c_p}{\rho} \). (iii) Levitated drop is quiescent and maintains nearly perfect spherical shape, simplifying the processes of accurately measuring the volume changes, the surface tension, and the viscosity. (iv) The system is equipped with a newly developed capability of measuring electrical resistivity by applying rotating magnetic field to a levitated sample. This capability has an additional implication for the indirect determination of thermal conductivity through the Wiedemann-Franz-Lorenz law, which relates the electrical resistivity with the thermal conductivity for certain metallic substances.

2. EXPERIMENTAL PROCEDURE

The HTESL levitates a sample 1 to 3 mm in diameter between a pair of parallel disk electrodes spaced about 12 mm apart (Fig. 1). In Fig. 1, the four small side electrodes around the bottom electrode control the sample position along horizontal direction, and the four coils positioned around the top electrode induce sample rotation. The electrode assembly is housed
by a stainless steel chamber which is typically evacuated to $10^{-8}$ Torr before sample heating begins. Samples are heated using a 1-KW xenon arc lamp. Detailed description of the HTESL is given in an earlier publication [1].

Once a levitated sample is molten, the melt shows very nearly spherical shape. In order to maintain clean surfaces during processing, it was necessary to begin with pure, clean samples. Germanium samples were prepared from 99.9999% pure stock from Johnson-Matthey. These were then ground roughly into spheres. They were cleaned by immersion in 5% hydrofluoric acid at room temperature for 5 minutes, rinsed in distilled water, and finally rinsed in anhydrous ethanol. The samples weighed approximately 20 mg.

Since the electrostatic levitation mechanism does not affect the sample temperature, a sample that is heated to a certain high temperature will cool purely radiatively when the heating source is blocked, and the ensuing cooling process can be described by the radiative heat transfer equation

$$mc_p \frac{dT}{dt} = -\sigma_{SB}e_T A(T^4 - T_E^4),$$  \hspace{1cm} (1)

where $m$ is sample mass, $c_p$ is the constant pressure specific heat capacity, $T$ is the sample temperature, $T_E$ is the environment temperature, $\sigma_{SB}$ is the Stefan-Boltzmann constant ($5.6705 \times 10^{-8}$ W·m$^{-2}$·K$^{-4}$), and $e_T$ is the hemispherical total emissivity. The fact that accurate measurement of $c_p/e_T$ is possible from Eq. (1) is one of the most important merits of the HTESL.

Measurements of the mass density and the specific heat capacity of molten germanium was initiated by blocking the heating source and allowing the germanium melt to cool until recalcitrance took place. Upon beam blocking, both the temperature measurement by a pyrometer and the image recording by a video system went on simultaneously throughout cooling process. A typical temperature versus time profile for a germanium melt obtained during such a cooling process is shown in Fig. 2. The melt started to cool from about 200 K above the melting temperature and undercooled approximately 60 K before recalcitrance took place. Upon recalcitrance the sample temperature rose sharply and reached isotherm state. It is interesting to note that, unlike the silicon case[2], Fig. 2 shows constant spectral emissivity over the isotherm region. Output of the single color pyrometer operating at 750 nm was calibrated using Planck's spectral distribution of emissive power taking the temperature immediately following the recalcitrance as its melting temperature ($T_{m}=1211$ K). 750 nm spectral emissivity of the melt over the entire liquid temperature range was assumed to be constant.
Temperature dependence of the mass density was measured by analyzing the video images taken during a cooling process. The image size was extracted from each video frame using an image analysis method which was developed in our laboratory [3].

To measure the surface tension, a low amplitude drop excitation field pulse was applied along the vertical direction and the transient drop oscillation following the pulse was recorded in a computer for later analysis. The drop excitation was done by applying an electric field pulse which varies sinusoidally at the drop resonance frequency. When the drop oscillation is sufficiently low in amplitude, one can utilize the Rayleigh's formula to determine the surface tension from the measured resonance frequency[4].

The surface charge on a levitated drop lowers the apparent surface tension, and the drop oscillation frequency reflects this. If we know the net drop charge, one can use the Rayleigh's expression for charged drop oscillation to extract the true surface tension $\sigma$ [5],

$$\omega = \left[ \frac{8\sigma}{\rho r_0^3} \left( 1 - \frac{Q^2}{16\pi r_0^2 \sigma} \right) \right]^{1/2},$$

(2)

where $\omega$ is the angular frequency of observed oscillation, $\rho$ is the mass density of the melt, $r_0$ is the radius of the melt when it is in spherical shape, and $Q$ is the net sample charge. Effects on surface tension due to non-uniform charge distribution and deviation from a perfect spherical shape were corrected using the perturbation analysis of electrostatically levitated drops which was derived by Feng and Beard [6].

3. MEASUREMENTS OF THE DENSITY AND THE THERMAL EXPANSION COEFFICIENT

Thermophysical properties of molten materials are intimately related to its density. The method we used in this work is basically an image analysis technique. This method consisted of (i) digitization of recorded video image, (ii) edge detection, (iii) calculation of the area (therefore, the volume of the sample) through linear spherical harmonic fit, and (iv) calibration of data with respect to a reference sphere for absolute values. The density was then obtained using the sample mass which was measured immediately following the experiment. Detailed description of the image analysis method used in this experiment was published elsewhere [3].

Fig. 3 shows the result of our density measurements of molten germanium over the temperature of 250 K. Unlike the density of molten silicon which showed pronounced quadratic behavior [2], the density of molten germanium rather shows a linear behavior which can be expressed in the following form:
\[
\rho_{\text{liq}}(T) = \rho_{\text{liq}}(T_m) + \frac{d\rho_{\text{liq}}}{dT}(T - T_m) \quad \text{Kg/m}^3,
\]

where the coefficients for the present result can be expressed by \(\rho_{\text{liq}}(T_m) = 5.67 \times 10^3 \text{ Kg/m}^3\) and \(d\rho_{\text{liq}}/dT = -5.42 \times 10^{-1} \text{ Kg/Km}^3\). The Table I compares the present work with three other works which could be found in the literature. \(\rho_{\text{liq}}(T_m)\) obtained by Lucas[7] using the bubble pressure method and by other workers using the pycnometer and volumetric measurement methods are about 2.3 \% smaller than the our result. On the other hand, the results obtained by sessile drop method by Khilya et al.[8] and also by Tavadse et al.[9] agree with the present work within 1.25 \%.

However, our temperature dependence of density shows \(\frac{d\rho}{dT}_{\rho} = -5.42 \times 10^{-1}\) Kg/Km\(^3\) which is 10 \% larger than the Lucas's, while it is approximately 13 \% smaller than those obtained by Khilya and Tavadse. Our result translates into the isobaric thermal expansivity \(\alpha = 9.656 \times 10^{-4} \text{ K}^{-1}\) which is reasonably in good agreement with ~0.9 given by Iida[10].

4. SPECIFIC HEAT MEASUREMENT

Constant pressure specific heat capacity is a very important thermodynamic parameter from which other parameters, such as enthalpy, entropy, and Gibbs free energy can be derived. In spite of their importance, specific heat capacity and hemispherical total emissivity are known for very few high-temperature liquids. Data are particularly scarce for the undercooled liquids since they tend to solidify when placed in contact with most crucibles. The HTESL allows determination of \(c_p/\varepsilon_T\) in a simple heat transfer environment while the levitated melt cools to undercooled states. Rearrangement of Eq. (1) gives

\[
\frac{c_p}{\varepsilon_T} = \frac{-\sigma_{SB}A(T^4 - T_e^4)}{m \frac{dT}{dt}}.
\]

Using temperature-time profile obtained experimentally (as shown in Fig. 2), and evaluating \(dT/dt\) from it, \(c_p/\varepsilon_T\) can be obtained as shown in Fig. 4. From this ratio \(c_p(T)\) can be determined if \(\varepsilon_T(T)\) is known, and conversely, \(\varepsilon_T(T)\) can be found if \(c_p(T)\) is known [11].

Frequently, specific heat values are known in many materials at their melting temperature, while the values for hemispherical total emissivity are not. In such cases, \(\varepsilon_T(T_m)\) at the melting temperature can be obtained. The literature value of the constant pressure specific
heat capacity of molten germanium at the melting temperature is $C_{p,liq}(T_m) = 27.61 \text{ J/mol K}$[12]. With this value together with the $c_p/\varepsilon_T$ shown in Fig. 4, the hemispherical total emissivity at the melting temperature $\varepsilon_T(T_m)$ is determined to be 0.17. This is in good agreement with Brekhovskikh's prediction that $\varepsilon_T(T)$ for the liquid will not exceed 0.18[13, 14].

Strictly speaking, in order to evaluate $c_p(T)$, the temperature dependence of $\varepsilon_T(T)$ has to be independently measured. Since $\varepsilon_T(T)$ is not available at the present time, let us assume that it remains constant at $\varepsilon_T(T) = \varepsilon_T(T_m) = 0.17$ over the liquid region of present interest, and evaluate $c_p(T)$ from Fig. 4. Such assumption may be a reasonable one if we consider the fact that the spectral emissivities of molten germanium at both visible and infrared wavelengths show almost no temperature dependence[15]. Fig. 5 shows $c_p(T)$ as a function of temperature so obtained. Like molten silicon[2], $c_p(T)$ of molten germanium also shows a non-linear behavior, decreasing with the increased temperature.

5. SURFACE TENSION

Spherical shape of a molten drop levitated by the HTESL greatly simplifies the surface tension measurements. In view of the fact that surface tension is particularly sensitive to even minute surface contamination, the high vacuum environment would be ideal for measuring surface tension, particularly of those chemically reactive materials.

For surface tension experiments we had to fix the sample temperature at a predetermined value until the surface tension data at that temperature was obtained. The pyrometer used for this experiment operated at 4 µm wavelength to avoid interference by the xenon arc-lamp radiation. As described in Section 2, a low amplitude electric pulse was applied along the vertical direction and the transient drop oscillation following the pulse was recorded in a computer. The electric field pulse has sinusoidal career frequency at the drop resonance frequency.

Fig. 6 shows our surface tension result on molten germanium as a function of temperature. The surface tension data can be expressed by

$$\sigma(T) = 583 - 0.08 (T - T_m) \text{ mN/m.} \quad (1160 \sim 1430 \text{ K}) \quad (5)$$

The surface tension 583 mN·m$^{-1}$ at the melting temperature is more than 6% smaller than 621 mN·m$^{-1}$ reported by Allen [16] and approximately 3% smaller than the value recently reported by Takamura[17]. As for $d\sigma(T)/dT$, the present result shows 0.08 mN·m$^{-1}$·K$^{-1}$ while Ref. [16] and [17] showed 0.26 mN·m$^{-1}$·K$^{-1}$ and 0.16 mN·m$^{-1}$·K$^{-1}$, respectively. At the present
time, it is too premature to prefer a particular result over others. Our levitation method in vacuum supposed to expose cleaner surface, yet it is surprising that our result show smaller surface tension than the reference values. Only more comprehensive experimental conditions in each of different experimental approaches would be able to reveal causes of such different results.

If we measure the decay time constants of transient free oscillation signals, we should be able to relate them to the viscosity of the melt through the following relationship[18]

\[
\frac{1}{\tau_2} = \frac{5\eta}{\rho r_o^2}.
\]

In Eq. (6), \(\tau_2\) is the time constant of exponentially decaying signal, \(\eta\) is the viscosity of the sample liquid, \(\rho\) is the density of the melt, and \(r_o\) is the radius of the drop. However, we discovered that the time constant we were measuring was highly sensitive to external perturbation forces. Such susceptibility to external noise is relatively more pronounced as the viscosity of the melt decreases. In the present case, the most dominant perturbing force was coming from the levitation force correcting the sample position 480 times per second. The viscosity data we obtained scattered between 0.13 mPascal-sec and 0.7 mPascal-sec. over the 1160 K \(\sim\) 1425 K range. In contrast, Glazov et al.[19] and Turovskii et al.[20] reported 0.78 mPascal-sec and 1.1 mPascal-sec for the viscosity at the melting point, respectively.

6. TEMPERATURE DEPENDENCE OF ELECTRICAL RESISTIVITY AND THERMAL CONDUCTIVITY

Electrical resistivity is known to be sensitive to reflect the state of local structures liquids. Utilizing the sample rotation capability which was newly built into the HTESL, the measurement of temperature dependence of electrical resistivity was attempted. To exert a torque to a levitated conducting sample, a rotating magnetic field was applied to the sample with its rotation axis coinciding with the gravitational field. The basic principle is same as the asynchronous motor in which the sample being investigated is the rotor. In fact, along with the four probe method, the rotating magnetic field method[10] is frequently used to measure electrical conductivity of molten material. Only difference between this method and our method is in the necessity of container which holds the sample liquid. The sample rotation method which can measure the electrical resistivity (or conductivity) of a molten sample which is levitated in a high vacuum by the HTESL is truly a non-contact method.

According to the principle of induction motor[21, 22], the torque \(\tau\) is given by
\[ \tau \propto \frac{s \tau_e}{r_e^2 + s^2 X^2}, \]  
(7)

where
\[ s \equiv \frac{\Omega - \omega}{\omega}, \]  
(8)

\( r_e \) is the electrical resistance of the rotor at a given temperature (the sample in the present case), \( X \) is the inductive reactance of the rotor, \( \omega_s \) is the angular frequency of applied field, and \( \omega \) is the instantaneous rotation frequency of the rotor. To make the Eq. (7) useful for the resistivity measurements, it is important to keep the amplitude of applied magnetic field experienced by the rotor stay constant for a given \( \omega_s \) throughout a resistivity measurement. In the present experiment on molten germanium, the condition \( r_e^2 \gg s^2 X^2 \) was satisfied to make the Eq. (7) even simpler, i.e.
\[ \tau \propto \frac{1}{r_e} \frac{\omega - \omega}{\omega_s}, \]  
(9)

Once the validity of Eq. (9) was experimentally verified using a molten aluminum drop, the resistivity of molten germanium was determined by measuring the torque of a levitated sample in the neighborhood of \( \omega = 0 \). Detailed description of this technique will be published elsewhere [23].

Since our intent is to measure the relative electrical resistivity of molten germanium over a certain temperature range, it requires a reference value at a known temperature. Keyes[24] reported \( r_{e,liq}(T_m) = 0.6 \, \mu\Omega m \), while 0.63 \( \mu\Omega m \) was reported by Domenicali[25], and 0.6 \( \mu\Omega m \) by Glazov[18]. If we choose \( r_{e,liq}(T_m) = 0.6 \, \mu\Omega m \) to calibrate our data, the our measured data can be expressed by the following equation:
\[ r_{e,liq}(T) = 0.6 + 1.18 \times 10^{-4} (T-1211.3) \, \mu\Omega m. \]  
(1211.3 - 1380 K)  
(10)

Fig. 7 shows our result along with the Glazov's work. While our data nicely fall onto a simple line, Glazov's data seem to show a rather complex structure. Whether such a structure has a physical meaning or it is simply an expression of uncertainties involved in his experiment is not known.

Since molten germanium is a metallic liquid where free electrons are responsible for the electrical and thermal conductivities, one can use the Wiedemann-Franz-Lorenz law to relate the thermal conductivity with the electric resistivity:
\[
\frac{\kappa_{ie}k_{liq}}{T} = \frac{\pi^2 k^2}{3e^2} \equiv L_o = 2.45 \times 10^{-8} \text{ W} \Omega \text{K}^{-2},
\]

(11)

where \(k\) is the Boltzmann constant and \(e\) is the electron charge. The constant \(L_o = \pi^2 k^2 / 3e^2\) is the Lorenz number whose validity was experimentally confirmed with high accuracy by Busch et al. [26].

Using the Eqs. (10) and (11), one can obtain the following expression for the thermal conductivity of molten germanium:

\[
\kappa_{liq}(T) = 49.43 + 2.90 \times 10^{-2} (T-1211.3) \text{ W m}^{-1} \text{K}^{-1}, \ (1211.3 \sim 1380 \text{ K})
\]

(12)

and Fig. 8 compares our result with two reference data available in the literature [22]. In this figure, the data by CINDA was obtained by converting the Glazov’s electrical resistivity data (see Fig. 7) using the Wiedemann-Franz-Lorenz law. Only the Filippov’s two data points were obtained through direct measurement of thermal conductivity. In Fig. 8 we can observe that the choice of \(r_{e,liq}(T_m) = 60 \, \mu \Omega\text{cm}\) as a reference point to calibrated our resistivity data was a reasonable one since it converts to thermal conductivity at melting point which agrees closely with other data. In contrast to other two reference data, our work shows increasing trend of thermal conductivity as the temperature increases. The sample rotation technique used in this work is very sensitive in detecting relative changes of resistivity as a function of temperature. Also, according to CINDA’s report, except molten germanium, other elements in Group IVA such as tin, lead, and silicon showed thermal conductivities which increased with increased temperature.

DISCUSSION

In this paper, we have reported for the first time various thermophysical properties of molten germanium using various non-contact diagnostic techniques which have been developed for the high temperature electrostatic levitator. The properties include the density, the thermal expansivity, the hemispherical total emissivity, the temperature dependence of constant pressure specific heat capacity, the surface tension, and the temperature dependence of electrical resistivity. The resistivity data was translated into the thermal conductivity using the Wiedemann-Franz-Lorenz law.

It was pointed out that the present technique measures the ratio \(c_{pl}/\varepsilon_T\), rather than independent measurement of \(\varepsilon_T\) and \(c_{pl}\). Therefore, only when valid \(c_{pl}\) at the melting temperature is available, \(\varepsilon_T\) can be determined with certainty.
We are surprised to see that our surface tension result smaller than the reference values as much as 3 ~ 6 %, although our germanium drop must have cleaner surface. We are planning to repeat this experiment in a near future. Also, it is worth pointing out that the present approach is not an adequate means of measuring the viscosity which is lower than ~ 1 mPascal-sec.

The electrical resistivity measuring technique is a new addition to our HTESL. At this point, it measures only relative changes of electrical resistivity although absolute measurement may be made possible in the future. Detailed description of this technique is beyond the scope of this paper, and it will be published elsewhere.

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REFERENCES
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Table I. Mass densities of molten germanium are compared.

<table>
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<th>$\rho_{\text{liq.}(T_m)} \times 10^3$ Kg/m$^3$</th>
<th>$d\rho_{\text{liq.}}/dT \times 10^{-1}$ Kg/Tm$^3$</th>
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<td>Lucas [7]</td>
<td>5.49</td>
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<td>Khilya et al. [8]</td>
<td>5.655</td>
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<td>Tavadse et al. [9]</td>
<td>5.598</td>
<td>- 6.25</td>
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<td>Present work</td>
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FIGURE CAPTION

Fig. 1. Schematic diagram of the electrode assembly used in the HTESL.

Fig. 2. A typical cooling profile of molten germanium drops as they undergo purely radiative cooling process.

Fig. 3. Density of molten germanium as a function of temperature.

Fig. 4. \( c_p/\varepsilon_T \) vs. temperature of molten germanium as calculated from data shown in Fig. 1.

Fig. 5. \( c_p(T) \) vs. temperature calculated from result shown in Fig. 4 assuming \( \varepsilon_T(T) = \varepsilon_T(T_m) = 0.17 \).

Fig. 6. Surface tension \( \sigma(T) \) of molten germanium as a function of temperature.

Fig. 7. Electrical resistivity of molten germanium as a function of temperature.

Fig. 8. Thermal conductivity of molten germanium obtained from Eq. (10) using the Wiedemann-Franz-Lorenz law along with existing reference data.
Top view

Top electrode

Coils (4)

Side view

Coils (4)

Sample

Side electrodes (4)

Bottom electrode

Fig-4
Fig. 3
Fig. 6