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Temperature Dependence of the Velocity of Sound in Liquid Metals of Group XIV

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The temperature dependences of the velocity of sound in liquid Pb, Sn, Ge, and Si have been measured by means of the pulse transmission technique over temperature ranges of 610–1078 K, 608–1463 K, 1215–1443 K, and 1723–1888 K, respectively. In both liquid Pb and Sn, the velocities of sound decrease linearly with increasing temperature, which is the same temperature dependence as shown in many other liquid metals. On the other hand, the velocities of sound in liquid Ge and Si exhibit anomalous temperature dependences. In Ge, the velocity of sound has a distinct maximum around 1280 K and decreases linearly at higher temperatures. In Si, the velocity of sound increases monotonically with increasing temperature in the temperature range investigated. It is considered that these results predict that the coordination numbers of liquid Ge and Si increase with increasing temperature.

KEY WORDS: adiabatic compressibility; germanium; lead; liquid metal; silicon; tin; velocity of sound.

1. INTRODUCTION

Mathematical modeling has been established as an exceedingly useful tool in improving process control and product quality. In order to improve models for the casting process, accurate thermophysical properties for the involved materials in liquid states are primarily required. The velocity of sound in liquid metals is one of the most important properties, which can

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be used to determine the basic thermodynamic properties such as adiabatic and isothermal compressibilities and the constant-volume heat capacity of liquid metals, provided that data are available for the constant-pressure heat capacity and coefficient of thermal expansion. Since the velocity of sound is also a sensitive structural property, the measurement of the velocity of sound in liquid metals is a valuable tool for studying the liquid structure.

The velocity of sound is generally independent of the frequency of ultrasonic waves used for the measurement. If it is assumed that the propagation of ultrasonic waves proceeds adiabatically and that the local fluctuation of liquid density due to the propagation of ultrasonic waves is negligibly small, the adiabatic compressibility β_S can be calculated from the velocity of sound v with the equation,

$$\beta_S = \frac{1}{\rho v^2} \tag{1}$$

where ρ is the density of the sample. In general, the velocity of sound in liquid metals decreases monotonically with increasing temperature. Since the densities of liquid metals of Group XIV decrease with increasing temperature [1], the decrease in the velocity of sound with temperature is considered to be due to the temperature dependences of the adiabatic compressibility. The thermal motion of the atoms leads to an increase in the nearest-neighbor separation, resulting in an increase in compressibility [2]. However, some liquid semi-metals and semiconductors exhibit anomalous behavior of the velocity of sound, which is generally regarded as a result of (i) structural reordering with a tendency toward a metal-like structure, and/or (ii) an increase in the density of free electrons [3]. Gitis and Mikhailov [4] have found that the velocity of sound in liquid antimony increases to a maximum at 1123 K and then falls off with a further increase in temperature. They have suggested that two structures are present near the melting point, having different coordination numbers corresponding, respectively, to the order of packing in the solid state and to a close-packed structure. An increase in the fraction of the close-packed structure results in a decrease in compressibility, whereas the thermal motion of the ions leads to an increase in compressibility. A minimum in compressibility and a maximum in sound velocity are thus produced by these two opposing processes. As stated above, the velocity of sound is closely related to the coordination structure. In spite of the aforementioned importance, however, only a few studies have been carried out on the velocity of sound in liquid metals [1].

The Group XIV elements (Pb, Sn, Ge, Si, C) are of practical as well as scientific importance. In particular, the structural and physical properties of liquid Si and Ge are essential for the study of single crystal growth from the melt. However, very little is known about the liquid phases of Si and Ge. The aim of the present study is to measure the temperature dependences of the velocity of sound in liquid metals of Pb, Sn, Ge, and Si so as to interpret the data from a structural viewpoint. Pb has a close-packed structure in both solid and liquid states [5]. Sn undergoes a solid-state phase transition from a diamond structure (α-Sn, grey tin) adopted at lower temperatures to a 6-fold-coordinated structure (β-Sn, white tin), and on melting, possesses a close-packed structure with a coordination number of 11 to 12 [5]. It is well-known that Ge and Si in the solid states adopt a tetrahedral diamond structure due to the sp^3 hybrid orbital. However, although it has been clarified by X-ray and neutron diffraction analyses that liquid Ge and Si have coordination numbers between 5 and 7, exhibiting metallic conduction, there is no consensus on their temperature dependences. The velocity of sound could be informative with respect to the structure of semiconductors in their liquid states.

2. EXPERIMENTAL

2.1. Principle

The pulse transmission technique [6] was employed in the present study. In this technique, pairs of buffer rods and transducers are used as shown in Fig. 1. Longitudinal acoustic pulses generated from the upper (or lower) transducer travel through the attached rod, the liquid, and the other rod in turn, and are received by the lower (or upper) transducer. The upper rod can be vertically shifted by a distance Δx, which is measured very accurately by, for instance, a micro-screw gauge or a cathetometer. The time required for a pulse to travel from one transducer to another can be measured by an oscilloscope. The velocity of ultrasonic waves (v) can be calculated by the ratio of the distance between two ends of the rods (Δx) and the time required for the transmission of the ultrasonic pulses (Δt);

$$v = \frac{\Delta x}{\Delta t} \tag{2}$$

2.2. Samples

Table I gives the supplier of the materials used in the present study together with their respective purities, as stated by the manufacturer. The samples were prepared from ca. 550 g of Pb shots, ca. 350 g of Sn shots,

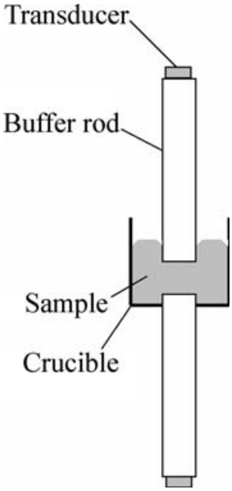

Fig. 1. Cell assembly of pulse transmission technique.

Table I. Materials Used in the Present Study

Material	Purity (%)	Supplier
Pb shots	99.99	Kanto Chemical Co.
Sn shots	99.97	Kanto Chemical Co.
Ge lumps	99.999	TDY Inc.
Si lumps	99.999	Nilaco Co.

ca. 260 g of Ge lumps, and ca. 110 g of Si lumps. Prior to the measurements, each sample was cleaned sequentially in an ultrasonic bath for 15 min with distilled water, anhydrous ethanol, and acetone.

2.3. Apparatus

Figure 2 shows a schematic diagram of the experimental apparatus. The experimental setup consists of an alumina crucible (60 mm in outer diameter, 50 mm in inner diameter, and 50 mm in height) containing the sample and two buffer rods (30 mm in diameter and 265 mm in length) made of high-density polycrystalline alumina. The crucible, which has a hole on the bottom with a slightly larger diameter than that of the rod, was cemented at the hole to the lower rod by means of an adhesive

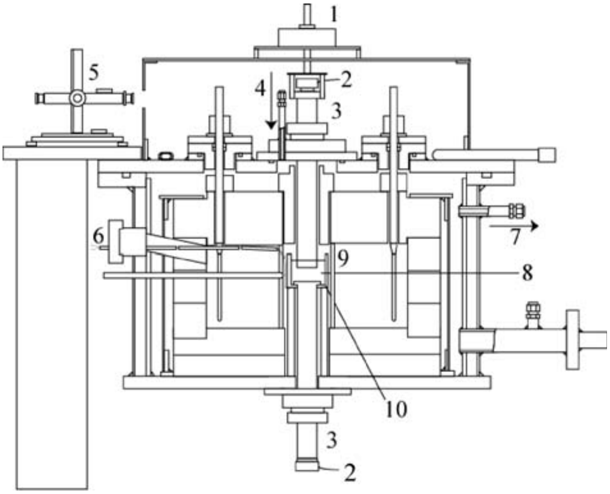

Fig. 2. Schematic diagram of the experimental apparatus: 1. Stepping motor, 2. Piezoelectric $BaTiO_3$ crystal, 3. Al_2O_3 buffer rod, 4. Gas inlet, 5. Cathetometer, 6. Thermocouple, 7. Gas outlet, 8. Liquid metal, 9. Al_2O_3 tube, 10. Al_2O_3 crucible.

composed mainly of zirconia and silica. Therefore, the rod can be directly attached to the liquid sample. The crucible was positioned in the even-temperature zone of the furnace. The piezoelectric transducers of $BaTiO_3$ crystal (12.7 mm in diameter) were fixed to the ends of the rods in line using the clamps, and glycerin was applied at the interfaces between the transducers and the rods to improve contact. The sample was heated by a furnace with Kanthal Super heating elements and melted in a flow of argon containing 10% hydrogen dehydrated by P_2O_5 to avoid surface oxidation of the sample; it is known that the transfer of acoustic energy into the liquid is often small because of the formation of surface oxidation, which yields poor adhesion between the buffer rod and the liquid. During the course of the experiments, the temperature of the liquid sample was measured using a Pt-13%Rh/Pt thermocouple, calibrated periodically and positioned in contact with the lower part of the alumina crucible.

Figure 3 shows a diagram of the electronic circuit used in the present study. A pulser-receiver (Panametrics-NDT, Model 5077PR) generated electrical signals (pulse voltage 400 V, pulse repetition rate 100 Hz), which were converted to longitudinal acoustic pulses by the upper transducer. The longitudinal acoustic pulses traveling through the liquid sample were converted to electrical signals by the lower transducer, which were detected

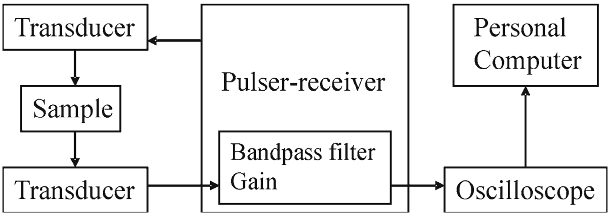

Fig. 3. Diagram of electronic circuit used in the present study.

and amplified by the same pulser-receiver, and displayed on an oscilloscope (Sony Tektronix, Model TDS520D).

2.4. Procedure

The liquid sample was held for at least 1 h at each measurement temperature before starting the measurement to confirm that the sample was at thermal equilibrium. The upper rod was shifted down vertically using a stepping motor so that the rod was immersed in the center of the liquid sample. Longitudinal acoustic pulses of 5 MHz were generated from the upper transducer, traveled through the attached rod, the liquid, and the other rod in turn, and were detected by the lower transducer in order to measure the time required for the transmission of the acoustic pulses. Subsequently, the distance between two ends of the rods was altered by changing the position of the upper rod, where the change in the distance (Δx) was measured by a cathetometer to an uncertainty of $10\,\mu$m. The transmission times were acquired at eight different distances between the two ends of the rods. Figure 4 shows a typical relationship between the values of Δx and Δt, obtained in measurements on liquid Pb at 1078 K. It can be seen that a good linear relationship has been obtained. A straight line was fitted to the data points using the least-squares method to obtain the velocity of sound from its slope.

In order to establish the feasibility of the sound-velocity measurement in liquid metals in the present study, the velocity of sound in liquid mercury was measured at room temperature. The obtained result of $1445\,\mathrm{m \cdot s^{-1}}$ is in good agreement with the reported value of $1453\,\mathrm{m \cdot s^{-1}}$ [7], i.e., within an experimental uncertainty of ±0.82%.

Measurements were carried out in the temperature ranges of 610–1078 K for Pb, 608–1463 K for Sn, 1215–1443 K for Ge, and 1723–1888 K for Si during the cooling cycle. Two runs were carried out for each element to ascertain the reproducibility. Reactions between the sample and the buffer rod were not observed after the measurements.

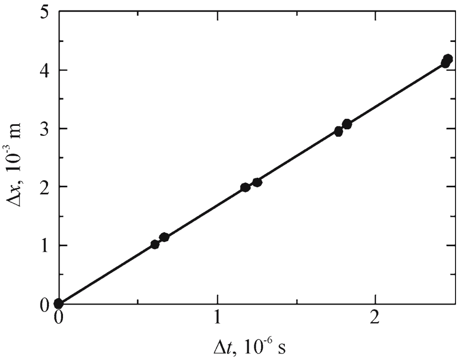

Fig. 4. Typical relationship between the values of Δx and Δt, obtained in measurements on liquid Pb at 1078 K.

3. RESULTS

Figures 5 through 8 show the temperature dependences of the velocity of sound in liquid Pb, Sn, Ge, and Si, respectively, in comparison with previous data [4,8–18]. Two different runs are represented by open and closed circles. Four to nine data points were taken for each run. The melting point of each element is indicated by the broken line with "m.p." The experimental uncertainty in the velocity of sound is $< \pm 1.0\%$. The method to estimate the uncertainties will be explained in Section 4. The present data for liquid Pb and Sn are in excellent agreement with reported values, except for those reported by Gordon [8] and Kleppa [9]. Both Gordon [8] and Kleppa [9] have employed the pulse echo technique, which has a drawback in that the main pulse is more likely to be affected by the trailing pulse generated by incoherent reflections from the surface of the rod [6]. In both liquid Pb and Sn, the velocity of sound is found to decrease linearly with increasing temperature. Gitis and Mikhailov [3] have proposed that a change in the temperature coefficient of the velocity of sound reflects a certain structural rearrangement. Therefore, the constant temperature coefficients of Pb and Sn are consistent with the fact that liquid Pb and Sn have a close-packed structure with a coordination number close to 12 independent of temperature. On the other hand, the velocities of sound in liquid Ge and Si exhibit anomalous temperature dependences. In Ge, the velocity of sound has a distinct maximum around 1280 K and decreases linearly at higher temperatures. In Si, the velocity of sound increases monotonically with increasing temperature in the temperature range investigated.

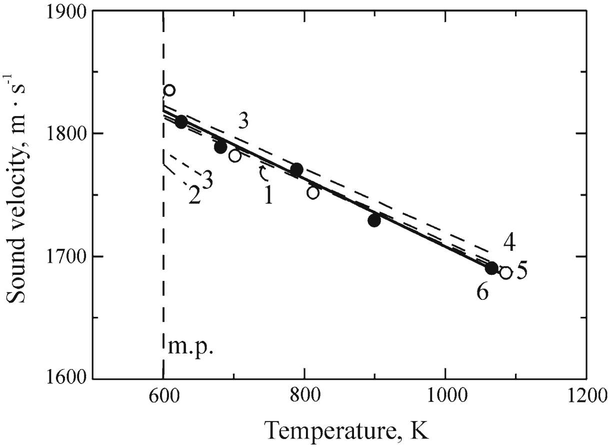

Fig. 5. Temperature dependence of the velocity of sound in liquid Pb. Open and closed circles represent two different runs. 1. Gitis and Mikhailov [4], 2. Gordon [8], 3. Kleppa [9], 4. Tsu et al. [10], 5. Koshigoe [11], 6. This study.

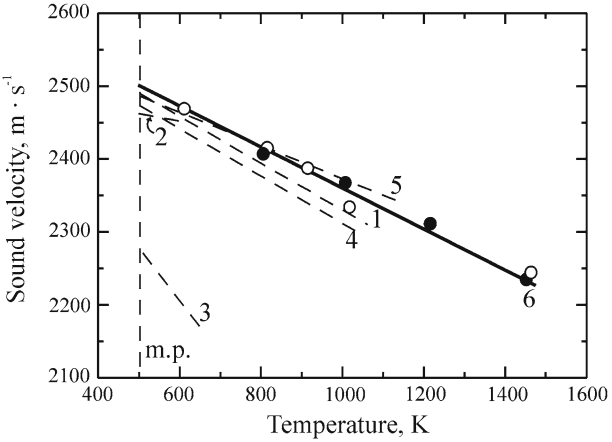

Fig. 6. Temperature dependence of the velocity of sound in liquid Sn. Open and closed circles represent two different runs. 1. Gitis and Mikhailov [4], 2. Gordon [8], 3. Kleppa [9], 4. Tsu et al. [10], 5. Koshigoe [11], 6. This study.

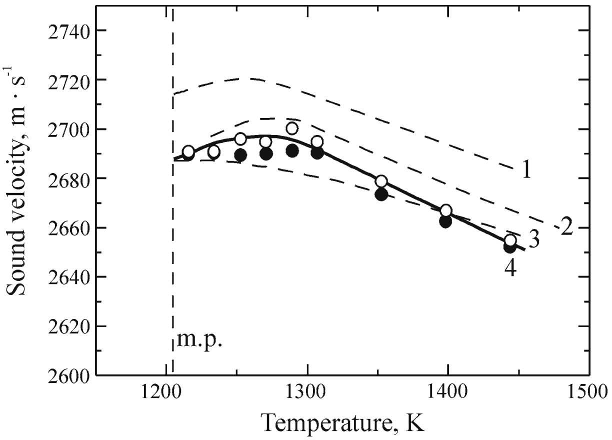

Fig. 7. Temperature dependence of the velocity of sound in liquid Ge. Open and closed circles represent two different runs. 1. Baidov and Gitis [12], 2. Glazov et al. [13], 3. Yoshimoto et al. [14], 4. This study.

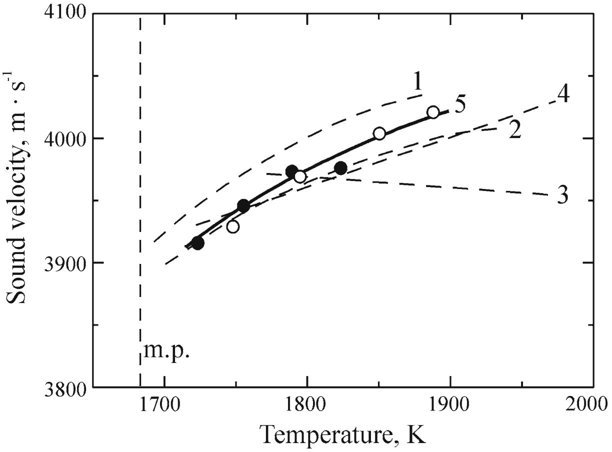

Fig. 8. Temperature dependence of the velocity of sound in liquid Si. Open and closed circles represent two different runs. 1. Yoshimoto et al. [15], 2. Glazov et al. [16], 3. Sokolov et al. [17], 4. Keita and Steinemann [18], 5. This study.

The following equations are recommended based on the results of the present study for the velocity of sound v as a function of temperature T (in K).

$$\text{Pb:} \quad v(\text{m} \cdot \text{s}^{-1}) = 1990 - 0.286T \quad (610 - 1078\,\text{K}) \tag{3}$$

$$\text{Sn:} \quad v(\text{m} \cdot \text{s}^{-1}) = 2630 - 0.269T \quad (608 - 1463\text{K}) \tag{4}$$

$$\text{Ge:} \quad v(\text{m} \cdot \text{s}^{-1}) = 891 + 2.88T - 1.15 \cdot 10^{-3}T^2 \quad (1215 - 1443\text{K}) \tag{5}$$

$$\text{Si:} \quad v(\text{m} \cdot \text{s}^{-1}) = -970 + 4.86T - 1.17 \cdot 10^{-3}T^2 \quad (1723 - 1888\text{K}) \tag{6}$$

The velocities of sound in liquid Pb, Sn, Ge, and Si at their melting points estimated by extrapolation of experimental results are 1820, 2490, 2690, and 3900 $\text{m} \cdot \text{s}^{-1}$, respectively.

4. DISCUSSION

4.1. Uncertainty in the Sound Velocity

The dominant uncertainty in the sound velocity stems from the following two factors; (1) the expected uncertainty in the sound-velocity value involved in one data point on the relationship between Δx and Δt, and (2) the standard deviations of eight sound velocity values, i.e., the standard deviations of the magnitude of the slope of the $\Delta x - \Delta t$ curve (see Fig. 4). The error due to the former factor ($\Delta v/v$) is calculated by taking the square root of the sum of the squared error in Δx, denoted by $\Delta(\Delta x)/\Delta x$, and the squared error in Δt, denoted by $\Delta(\Delta t)/\Delta t$:

$$|\Delta v/v| = \sqrt{\left(\Delta(\Delta x)/\Delta x\right)^2 + \left(\Delta(\Delta t)/\Delta t\right)^2} \tag{7}$$

It is calculated to be $< \pm 0.5\%$, where the errors in Δx and Δt were estimated, by dividing the average length change of an alumina buffer rod due to the heating of the rod (0.02 mm) by the average pulse transmission distance (20 mm), to be 0.1%, and by dividing the time resolution of oscilloscope (0.004 μs) by the average pulse transmission time (1 μs), to be 0.4%, respectively. On the other hand, the standard deviations of eight sound-velocity values are calculated as $< \pm 1.0\%$, which is larger than the expected uncertainty in one sound-velocity measurement.

4.2. Anomalous Temperature Dependences of the Velocity of Sound in Liquid Ge and Si

Figure 9 shows the adiabatic compressibilities β_S for four elements calculated from the measured velocities of sound and the reported density values [1] using Eq. (1). For Pb and Sn, the adiabatic compressibility increases monotonically with temperature, which is due to the greater mean separation between ions with increasing temperature [3]. In contrast, the adiabatic compressibility in liquid Ge remains constant at temperatures not too far from the melting point and increases with temperature at higher temperatures, and that in liquid Si decreases monotonically with increasing temperature over the whole temperature range investigated.

With respect to anomalous temperature dependences of the compressibility shown in some semi-metals and semiconductors in their liquid states, Gitis and Mikhailov [3] have suggested that a decrease in compressibility with increasing temperature could be relevant to an increase in the number density of free electrons with increasing temperature. However, it has been reported that the Hall coefficient of liquid Si remains constant as $-3.3 \cdot 10^{-11}\,\mathrm{m}^3 \cdot \mathrm{C}^{-1}$ in the vicinity of its melting point independent of temperature, which is in good agreement with the calculated value using

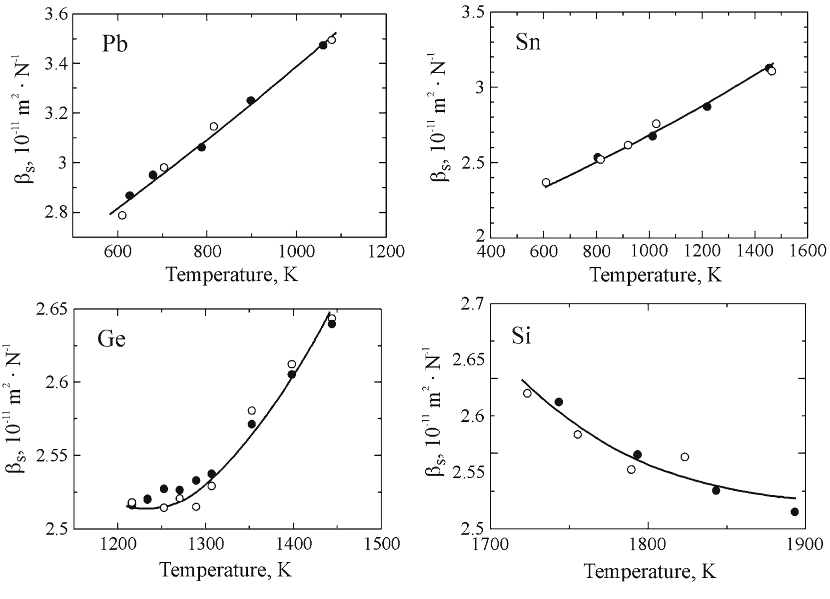

Fig. 9. Adiabatic compressibilities for four elements calculated from the measured velocities of sound and reported density values [1].

the theory of free electrons and assuming that Si releases four valence electrons per atom [19]. Therefore, the change in the number density of free electrons is not the reason for the anomalous temperature dependences of the compressibility.

Baidov and Gitis [12] have proposed that an increase in the coordination number would also compensate for the increase in the compressibility attributed to an enhancement of the thermal motion of atoms. The coordination numbers of liquid Ge and Si obtained by X-ray and neutron diffraction analyses [20–28] vary widely between 5 and 7 among different studies, and the distinct temperature dependences cannot be deduced by a comparison of these reported values. On the other hand, Kresse and Hafner [29] have carried out *ab initio* molecular-dynamics simulation, and have reported that the average coordination number of liquid Ge is 5.8, while that of supercooled liquid Ge is 4.63. If it is assumed that supercooled liquids have the same properties and structures as normal liquids, their results imply that the coordination numbers of liquid Ge increases with increasing temperature, which is compatible with the results of the present study according to the idea of Baidov and Gitis [12]. As with liquid Ge, liquid Si is considered to have a larger coordination number as the temperature increases based on our experimental results.

5. CONCLUSIONS

Temperature dependences of the velocity of sound in liquid Pb, Sn, Ge, and Si have been measured by means of the pulse transmission technique. Table II summarizes all the results. The following equations have been obtained for the velocity of sound v as a function of temperature T (in K). Pb: $v(\mathrm{m \cdot s^{-1}}) = 1990 - 0.286T$ (610 – 1078 K), Sn: $v(\mathrm{m \cdot s^{-1}}) = 2630 - 0.269T$ (608 – 1463 K), Ge: $v(\mathrm{m \cdot s^{-1}}) = 891 + 2.88T - 1.15 \cdot 10^{-3}T^2$ (1215–1443 K), and Si: $v(\mathrm{m \cdot s^{-1}}) = -970 + 4.86T - 1.17 \cdot 10^{-3}T^2$ (1723 – 1888 K). The velocities of sound in liquid Pb, Sn, Ge, and Si at their melting points have been estimated by extrapolation of experimental results as 1820, 2490, 2690, and 3900 $\mathrm{m \cdot s^{-1}}$, respectively. It is considered that the anomalous temperature dependences of the velocity of sound in liquid Ge and Si indicate that the coordination numbers of the liquids increase with an increase in temperature.

Table II. Measured Velocities of Sound ($m \cdot s^{-1}$)

	Pb		Sn		Ge		Si	
	Temp. (K)	Velocity of sound	Temp. (K)	Velocity of sound	Temp. (K)	Velocity of sound	Temp. (K)	Velocity of sound
Run 1	626	1810.5	804	2408	1216	2690.9	1723	3916.1
	678	1790.3	1012	2366	1233	2690.8	1755	3945.9
	787	1769.8	1218	2306	1252	2689.5	1789	3973.3
	897	1729.8	1453	2234	1270	2692	1823	3976.3
					1289	2690.8		
					1307	2690.6		
					1352	2673.6		
					1398	2662.8		
					1443	2652.5		
Run 2	610	1834	608	2470	1216	2689.9	1748	3929
	703	1784	814	2416	1233	2691.1	1795	3969
	814	1749	919	2379	1252	2696.2	1852	4003
	1078	1688	1025	2332	1270	2695	1889	4020
			1463	2242	1289	2700.4		
					1307	2695		
					1352	2678.4		
					1398	2666.3		
					1443	2654.4		

REFERENCES

1. T. Iida and R. I. L. Guthrie, *The Physical Properties of Liquid Metals* (Oxford University Press, 1988), p. 91.
2. W. P. Mason, *Physical Acoustics*, Vol. IV, Part B (Academic Press, New York, 1968), p. 57.
3. M. B. Gitis and I. G. Mikhailov, *Sov. Phys. Acoust.* **12**:14 (1966).
4. M. B. Gitis and I. G. Mikhailov, *Sov. Phys. Acoust.* **11**:372 (1966).
5. J. P. Gaspard, Ph Lambin, C. Mouttet, and J. P. Vigneron, *Philos. Mag. B* **50**:103 (1984).
6. T. Matsushita, M. Hayashi, and S. Seetharaman, *Int. J. Mater. Prod. Technol.* **22**:351 (2005).
7. J. L. Hunter, T. J. Welch, and C. J. Montrose, *J. Acoust. Soc. Am.* **35**:1568 (1963).
8. R. B. Gordon, *Acta Met.* **7**:1 (1959).
9. O. J. Kleppa, *J. Chem. Phys.* **18**:1331 (1950).
10. Y. Tsu, Y. Shiraishi, K. Takano, and S. Watanabe, *Nippon Kinzoku Gakkai* **43**:439 (1979).
11. F. Koshigoe, *Master's Thesis* (Tokyo Institute of Technology, 1999).
12. V. Baidov and M. Gitis, *Sov. Phys. Semicond.* **4**:825 (1970).
13. V. Glazov, A. Aivazov, and V. Timoshenko, *Sov. Phys. Solid State* **18**:684 (1976).
14. N. Yoshimoto, H. Shibata, M. Yoshizawa, K. Suzuki, K. Shigematsu, and S. Kimura, *Jpn. J. Appl. Phys.* **35**:2754 (1996).
15. N. Yoshimoto, M. Ikeda, M. Yoshizawa, and S. Kimura, *Physica B* **219&220**:623 (1996).

16. V. M. Glazov, S. G. Kim, and K. B. Nurov, *Sov. Phys. Semicond.* **22**:202 (1988).
17. L. N. Sokolov, Y. L. Kats, and G. N. Okorokov, *Izv. Akad. Nauk SSSR Met.* **4**:62 (1977).
18. N. Keita and S. Steinemann, *Phys. Lett.* **72A**:153 (1979).
19. V. M. Glazov, V. B. Koltsov, and V. A. Kurbatov, *Sov. Phys. Semicond.* **22**:202 (1988).
20. M. C. Bellissent-Funel and R. Bellissent, *J. Non-Cryst. Solids* **65**:383 (1984).
21. J. P. Gabathuler and S. Steeb, *Z. Naturforsch* **34a**:1314 (1979).
22. Y. Waseda and K. Suzuki, *Z. Physik B* **20**:339 (1975).
23. P. S. Salmon, *J. Phys. F: Met. Phys.* **18**:2345 (1988).
24. S. P. Isherwood, B. R. Orton, and R. Manaila, *J. Non-Cryst. Solids* **8–10**:691 (1972).
25. H. Kimura, M. Watanabe, K. Izumi, T. Hibiya, D. Holland-Moritz, T. Schenk, K. R. Bauchspieβ, S. Schneider, I. Egry, K. Funakoshi, and M. Hanfland, *Appl. Phys. Lett.* **78**:604 (2001).
26. Y. Waseda, K. Shinoda, K. Sugiyama, S. Takeda, K. Terashima, and J. M. Toguri, *Jpn. J. Appl. Phys.* **34**:4124 (1995).
27. S. Ansell, S. Krishnan, J. J. Felten, and D. L. Price, *J. Phys.: Condens. Matter* **10**:L73 (1998).
28. I. Stich, M. Parrinello, and J. M. Holender, *Phys. Rev. Lett.* **76**:2077 (1996).
29. G. Kresse and J. Hafner, *Phys Rev. B* **49**:14251 (1994).