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## Electrical resistivity and thermopower of liquid Ge and Si

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**Abstract.** The electrical resistivity  $\rho$  and thermopower  $S$  of pure liquid silicon and pure liquid germanium have been carefully measured. For silicon, a new containment material was used, namely high-density graphite. This graphite has a low thermopower ( $6 \mu\text{V}^\circ\text{C}^{-1}$  at  $1500^\circ\text{C}$ ) a high resistivity ( $1000 \mu\Omega \text{ cm}$  at  $1500^\circ\text{C}$ ), and little or no reaction with Si, making it an ideal containment material. The results for each liquid show a metallic value of resistivity, a small but positive temperature coefficient of the resistivity and a small thermopower. In particular, for liquid Si,  $\rho = 75.2 \pm 0.6 \mu\Omega \text{ cm}$ ,  $d\rho/dT = (1.7 \pm 0.9) \times 10^{-2} \mu\Omega \text{ cm}^\circ\text{C}^{-1}$  and  $S = -2.1 \pm 0.6 \mu \text{ V}^\circ\text{C}^{-1}$  and, for liquid Ge,  $\rho = 66.8 \pm 0.2 \mu\Omega \text{ cm}$ ,  $d\rho/dT = (2.7 \pm 0.2) \times 10^{-2} \mu\Omega \text{ cm}^\circ\text{C}^{-1}$  and  $S = -0.3 \pm 0.5 \mu \text{ V}^\circ\text{C}^{-1}$ ; all values are for the respective melting temperatures of Si and Ge. We also report a calculation of the resistivity of each liquid, using the Ziman formalism, with a recent pseudopotential and an experimental structure factor. Both our experimental and our calculated results are compared with other work.

### 1. Introduction

The properties of liquid Si ( $\ell$ -Si) and liquid Ge ( $\ell$ -Ge) have recently become the focus of new attention with the advent of successful new computing techniques which are yielding results previously unavailable. Among the unusual characteristics of these liquids which the new theoretical methods address are neutron and x-ray structure factors  $A(Q)$ , with a substantial shoulder on the high- $Q$  side of the main peak, yielding a radial distribution function with a first-nearest-neighbour coordination as low as 5 [1]; a value of approximately 12 is normally associated with a close-packed simple liquid structure. This low co-ordination implies an open structure and perhaps indicates that some remnants of the crystalline tetrahedral network remain. Early attempts to explain the structure factor of these liquids with multiple-diameter hard-sphere modelling [2] reproduced the first peak of  $A(Q)$  fairly well, but became worse at higher  $Q$ . Other attempts suggests two kinds of coordination, with some of the atoms being fourfold co-ordinated and some being close packed [3]. More recently, Jank and Hafner [4] calculated the structure of these liquids, using pseudopotential perturbation theory (PPT) with a simple local Ashcroft pseudopotential; they concluded that the unusual coordination numbers of  $\ell$ -Si and  $\ell$ -Ge are a result of Freidel oscillations superimposed on the repulsive hump of the interatomic potential, and that the balance of volume energy and this potential leads to the splitting of the first coordination shell. The results for this calculation of the structure factor are in good agreement with the especially interesting new work of Stich *et al* [5], who have followed an *ab-initio* approach, working from local density functional

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(LDF) theory and using standard equations of motion for the ionic and for the electronic degrees of freedom. In addition to  $A(Q)$ , their model yields information on the electronic charge density dynamics; this displays a build-up of charge between neighbouring atoms in  $\ell$ -Si that is interpreted with the aid of the triplet coordination function as the remnants of tetrahedral bonding in the liquid. Further study of  $\ell$ -Ge by Kresse and Hafner [6] using the LDF has validated the earlier PPT study [4] and has also produced a self-diffusion coefficient that agrees well with experiment.

These computer models have also shown that the density-of-states (DOS) function of silicon becomes metallic and nearly free electron like upon melting in spite of the unusual coordination [4, 7], losing the sharp features associated with  $sp^3$  bonding in the solid. Although measured ultraviolet photoemission spectra have shown that the DOS for  $\ell$ -Ge has a minimum between the s and p states [8], the minimum is well away from  $E_F$  (calculated from nearly-free-electron theory) and is not expected to affect the electronic transport properties.

Evidence such as this would suggest that the Ziman [9] theory, with an adequate pseudopotential and an accurate structure factor, could provide a relatively good calculation of the electronic transport properties for these liquids. In the Ziman formulation, the resistivity  $\rho$  for a pure liquid metal may be written

$$\rho = \frac{3\pi}{e^2\hbar v_F^2} \frac{N}{V} \frac{1}{4k_F^2} \int_0^{2k_F} Q^3 A(Q) |u(Q)|^2 dQ \quad (1)$$

where  $u(Q)$  is the screened pseudopotential,  $A(Q)$  is the structure factor and  $Q$  is the magnitude of the scattering vector. The thermopower is related to the logarithmic derivative of the resistivity:

$$S = \frac{+\pi^2 k_B T}{3|e|} \left( \frac{\partial \{\ln[\rho(E)]\}}{\partial E} \right)_{E=E_F} \quad (2)$$

Improving theoretical (including molecular dynamics) techniques and more satisfactory pseudopotentials have created a demand for higher-quality measurements of the electronic properties of  $\ell$ -Si and  $\ell$ -Ge. Differences of about 20% between measured values of these properties by various workers make new and accurate measurements desirable. Here we present new measurements of  $\rho$  and  $S$  for these liquids that carry uncertainties of less than 1% for  $\rho$  and less than  $0.6 \mu\text{V}^\circ\text{C}^{-1}$  for  $S$ .

## 2. Experimental method

The experimental method used to study  $\ell$ -Ge has been described in detail elsewhere [10]. The only modification to this is the addition of graphite plugs, used to seal the contact holes in the containment tubes; these more securely contain the liquid and allow electrical contact to be made to the sample.  $\ell$ -Ge can be contained easily in high-density  $\text{Al}_2\text{O}_3$  tubes with no evidence of attack, as is apparent from visual inspection, from the stability of the measurements and from the ease of separation of the solid sample from the post-experiment tube. The resistivity was measured by the four-probe DC technique. The thermopower of germanium was measured relative to chromel counterelectrodes;  $S(T)$  for chromel is from [10].

Numerous attempts have been made to measure the resistivity of  $\ell$ -Si; we attribute some of the great disparity in the measurements to contamination of the samples due to containment in  $\text{Al}_2\text{O}_3$  crucibles; we consider that all such measurements should be treated with caution because of serious corrosion that we have noted in our tests of  $\ell$ -Si in  $\text{Al}_2\text{O}_3$ .

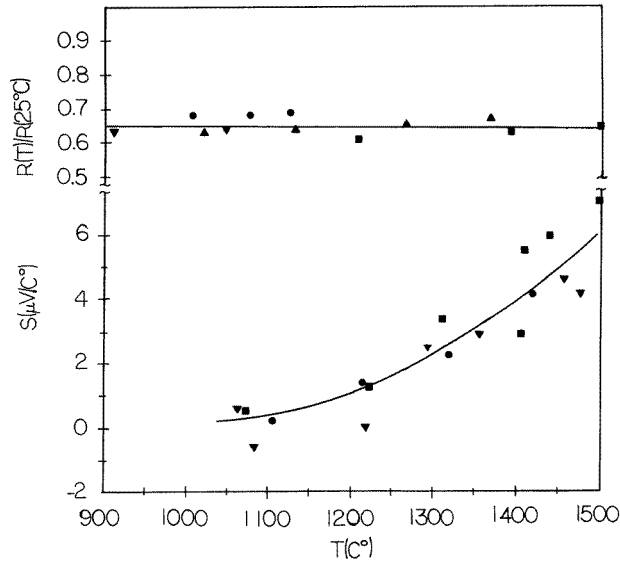
One recent measurement of  $\rho$  was done on a sample held in a boron nitride container [11]; we expect that this should provide a much better result. We find only one attempt to measure the thermopower of  $\ell$ -Si [12]; this measurement was conducted in an  $\text{Al}_2\text{O}_3$  container and must therefore also be treated with care.

Because of the great difficulty usually experienced in containing  $\ell$ -Si, we shall describe our method in some detail. We found that we were able to contain this liquid very well within high-density graphite, which allowed us to sidestep the oxidation problems that plague experiments done in quartz or alumina containers. Other workers have found that conventional machined graphite rods immersed in  $\ell$ -Si experience a change in radius due to corrosion of only about  $1.02 \times 10^{-3} \text{ cm h}^{-1}$  [13]; for our experimental containers this would result in about a 2% change in the cross-sectional area of the sample over the course of an average experiment. Further, these workers discovered that x-ray diffraction measurements on the boundary between  $\ell$ -Si and graphite display no evidence of diffraction peaks that would indicate the presence of silicon carbide [13]. (If an insulating layer of SiC were to form at this interface, it would prevent measurement of the transport properties.) In a separate test, we have measured the resistance of a graphite- $\ell$ -Si-graphite junction for as long as 12 h and have seen no increase in the resistance, implying no measurable formation of SiC.

The previous tests done by other workers (noted above) were on graphite prepared by an unknown method and characterized only by some indication of its hardness (6–7 on the Mohs scale) and low porosity. Our graphite was supplied by ESPI, and was their Aeromet grade. This is the hardest, least porous graphite that they make and appears to be at least as good for containing  $\ell$ -Si as the previously tested material.

Not only are the containment properties of this graphite very good, but its electronic properties make it a nearly ideal sample holder at these temperatures. In particular, this material has a low thermopower (about  $6 \mu\text{V } ^\circ\text{C}^{-1}$  at  $1500^\circ\text{C}$ ) and a high resistivity (about  $1000 \mu\Omega \text{ cm}$  at  $1500^\circ\text{C}$ ). Tests of the resistivity and thermopower of Aeromet-grade graphite from room temperatures to  $1600^\circ\text{C}$  were conducted on numerous rods of different batch numbers, and several individual graphite rods were tested throughout the full range of temperature several times. Although the resistivity varied by about 10% from one rod to the next, the ratio  $\rho(T)/\rho$  (room temperature) was highly reproducible. The thermopower of the graphite, however, was consistent to within  $\pm 1 \mu\text{V } ^\circ\text{C}^{-1}$  on all rods tested. Standard curves were established on the basis of these tests so that a calibration for each tube constant could be done with mercury at room temperature, and the parameters of the tube at high temperatures could be computed. Plots of the calibration data are presented in figure 1.

To form each graphite tube, a graphite rod was drilled with a special hollow core drill, leaving a wall thickness of about 0.76 mm; triangular grooves for placement of contact wires were machined around its surface to a depth of about 0.20 mm. Voltage leads for resistivity measurements were made with Mo wires of nominal 0.102 mm diameter placed in these grooves and held in place with alumina clamps. The uncertainty introduced into the measurement by the machining of the grooves was estimated at below 0.1%. The thermocouples used for temperature measurement were W–5% Re and W–26% Re, were supplied in matched lengths by Omega Engineering Inc. and were quoted to be accurate to  $\pm 1\%$ . The W–26% Re leg also served as the counterelectrode for measurement of  $S$ , and its thermopower was measured to  $1500^\circ\text{C}$  against Pt, using the results of Roberts *et al* [14] for Pt. Further calibration of W–26% Re below  $1200^\circ\text{C}$  was conducted against chromel, with the thermopower of chromel taken from [10]. Moreover, these calibrations were also compared with data obtained from the thermocouple voltage curve for W versus W–26% Re published by Omega Engineering Inc, using data from Roberts *et al* [14] for



**Figure 1.**  $R(T)/R$  (room temperature) and thermopower of ESPI Aeromet-grade high-density graphite. The thermopower was measured with W-26% Re counterelectrodes. The various symbols signify different graphite rods tested in separate experiments.

$S(T)$  for W. Our best fit to these data for W-26% Re is

$$S_{W-Re}(T) = -3.98582 + 6.91069 \times 10^{-2}T - 2.93294 \times 10^{-6}T^2 \mu\text{V}^\circ\text{C}^{-1} \quad (3)$$

for the range of temperatures from 1000 to 1500 °C. We estimate the uncertainty in  $S$  to be  $\pm 0.5 \mu\text{V}^\circ\text{C}^{-1}$  for this material.

Values for  $\rho$  and  $S$  for  $\ell$ -Si were extracted from measured data by considering the  $\ell$ -Si and the graphite tube as parallel conductors. A ‘small-thermal-gradient method’ was used to obtain the relative thermopower  $dV/dT$  of the parallel combination. The thermopower  $S$  of the liquid was then obtained from the relation

$$S_1 = (1 + B)(S_x + dV/dT) - BS_t \quad (4)$$

where  $S_x$  is the thermopower of the counterelectrode (here W-26% Re),  $S_t$  is the thermopower of the graphite tube and

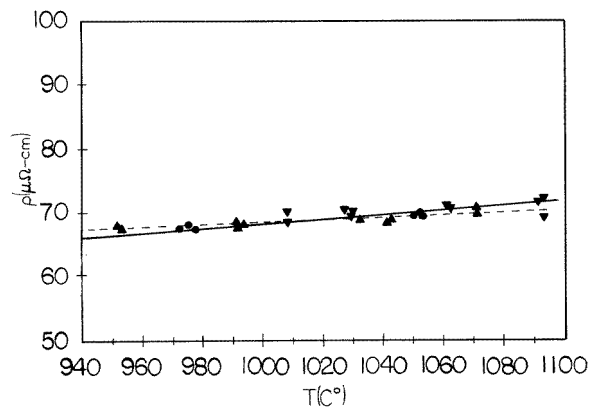
$$B = \rho_1 A_t / \rho_t A_1 \quad (5)$$

where  $A_t$  and  $A_1$  are the cross-sectional areas of the tube and the sample, respectively, and  $\rho_t$  and  $\rho_1$  are their resistivities. Because of the dimensions chosen for the tube and because of its electronic properties, the value of  $B$  in these experiments was only about 0.02; the contribution of  $B$  to the measured thermopower of the parallel system was therefore also very small, only about  $0.12 \mu\text{V}^\circ\text{C}^{-1}$ . As a result, uncertainties in the tube parameters contributed minimally to the final values obtained for  $S$  for  $\ell$ -Si.

Germanium and silicon sample materials were supplied by Aesar-Johnson Matthey Co. and were of 99.9999% and 99.99% purity, respectively. All measurements were done in a system baked under vacuum and backfilled with argon.

### 3. Results

Our experimental results for  $\ell$ -Ge are shown in figures 2 and 3 and those for  $\ell$ -Si are shown in figures 4 and 5; these are also summarized in table 1, with some previous results. Both  $\ell$ -Si and  $\ell$ -Ge have the characteristics of metallic behaviour: fairly small values of resistivity, positive temperature slope of the resistivity and small thermopower. We made measurements on three separate samples of  $\ell$ -Ge; as can be seen in the figures, all the results are very consistent with one another. By making a least-squares linear fit to *all* our data we find  $\rho(\ell\text{-Ge})$  at the melting point ( $938^\circ\text{C}$ ) to be  $66.8 \pm 0.2 \mu\Omega \text{ cm}$  and  $d\rho/dT = (2.7 \pm 0.2) \times 10^{-2} \mu\Omega \text{ cm } ^\circ\text{C}^{-1}$ . These values agree exceptionally well with the most recent results reported by Koubaa *et al* [15] (see table 1); we note also that these workers contained their sample in alumina and measured resistivity with the direct-contact four-probe technique. In addition, our results for the thermopower,  $(-0.3 \pm 0.5) \mu\text{V } ^\circ\text{C}^{-1}$ , are also in good agreement with those of the same workers, as well as other recent work (see table 1).

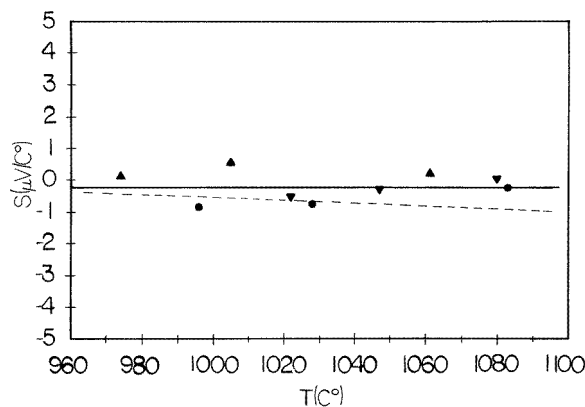


**Figure 2.** The electrical resistivity of  $\ell$ -Ge. Only a fraction of our resistivity points are shown for better graphical clarity, and different symbols signify separate samples. The results of Koubaa and Gasser [15] are shown as a broken line.

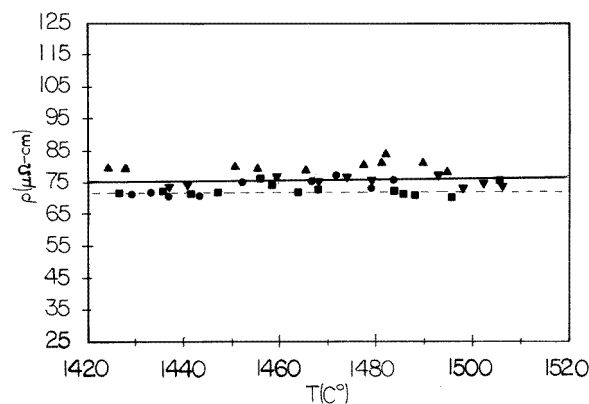
Our value of  $\rho(75.2 \pm 0.6 \mu\Omega \text{ cm}$  at  $T_{mp} = 1410^\circ\text{C}$ ) for  $\ell$ -Si, also obtained by a least-squares fit to all data, is very close to the recent value of Sasaki *et al* [11], who also used a four-probe measurement technique with boron nitride containment. As is evident in figure 4, one of our sets of measurements of resistivity of  $\ell$ -Si was somewhat higher than the others; the uncertainty and final value quoted include all the data. Using all our measurements of  $\ell$ -Si, the slope of the resistivity is  $(1.8 \pm 0.9) \times 10^{-2} \mu\Omega \text{ } ^\circ\text{C}^{-1}$ . The measured thermopower of  $\ell$ -Si was very consistent through all experiments (three different samples); our value of  $-2.1 \pm 0.6 \mu\text{V } ^\circ\text{C}^{-1}$  differs substantially from the earlier work of Glazov *et al* [12], however. We consider this difference a result of our improved containment method. (Containment for this earlier measurement was  $\text{Al}_2\text{O}_3$ .)

### 4. Discussion

It is clear that our primary goal in this research, that of obtaining high-quality measurements of  $\rho$  and  $S$  for the  $\ell$ -Ge and  $\ell$ -Si, has been met. It will now be interesting to discover



**Figure 3.** The thermopower of  $l$ -Ge. The results for the three samples are shown with different symbols. The experimental thermopower of Koubaa and Gasser [15] is shown as a broken line.

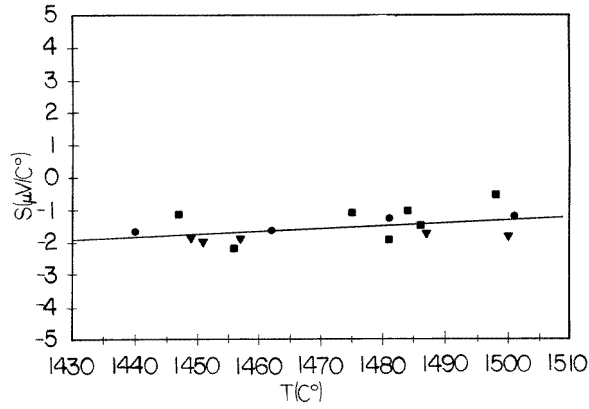


**Figure 4.** The electrical resistivity of  $l$ -Si. Again, only a fraction of the resistivity points taken are shown, and results from four samples measured by the same method are shown as different symbols. For comparison, the results of Sasaki *et al* [11] are shown as a broken line.

how successfully various theoretical methods can reproduce these values for the electronic transport parameters. (Numerical results of these calculations are shown in table 2.)

Some early calculations of  $\rho$  and  $S$  for  $l$ -Ge and  $l$ -Si [16, 17] were relatively successful, utilizing the Ziman method and either a modified hard-sphere structure factor [17] or an experimental structure factor [16]. (In [16] the Ge  $A(Q)$  was used in the calculations for Si; the results for this calculation of  $\rho$  and  $S$  were not nearly so good.) Their success is somewhat surprising, especially in the case of Rahman [17], since the softened hard-sphere structure factor used in that work inadequately describes the shoulder seen in the experimental scattering data [18, 19]. Other workers [11, 18, 20] have used the extended Ziman formulae, a  $t$ -matrix method developed especially to address the transition metals, and an experimentally determined  $A(Q)$ . The results of these calculations come very close to the measured values of these parameters in each case (see table 2).

Koubaa and Gasser [15] have recently attempted a calculation for  $l$ -Ge, again utilizing a pseudopotential in the Ziman formalism, but have chosen the Bachelet–Haman–Schluter



**Figure 5.** The thermopower of  $\ell$ -Si. The different symbols denote different samples.

**Table 1.** Experimental values for  $\rho$ ,  $d\rho/dT$ ,  $S$  and  $dS/dT$  for  $\ell$ -Ge and  $\ell$ -Si at their respective melting temperatures. (The numbers in the square brackets identify the references.)

Metal	$\rho$ ( $\mu\Omega$ cm)	$d\rho/dT$ ( $10^{-2} \mu\Omega$ cm $^{\circ}\text{C}^{-1}$ )	$S$ ( $\mu\text{V}^{\circ}\text{C}^{-1}$ )	$dS/dT$ ( $10^{-3} \mu\text{V}^{\circ}\text{C}^{-2}$ )
Ge	$66.8 \pm 0.2$ [present]	$2.7 \pm 0.2$ [present]	$-0.3 \pm 0.5$ [present]	$0 \pm 5$ [present]
	67.8 [15]	1.3 [15]	-0.4 [15]	-4 [15]
	66 [26]	$\simeq 1.5$ [28]	-0.5 [20]	-3.3 [20]
	85 [27]		0 [27]	
	80 [28]			
Si	$75.2 \pm 0.6$ [present]	$1.7 \pm 0.9$ [present]	$-2.1 \pm 0.6$ [present]	$9.1 \pm 5.3$ [present]
	72 [11]	(non-linear) [11]	-14 [12]	
	60 [27]			
	80 [26]	$\simeq 6$ [12]		
84 [12]				

(BHS) [21] non-local pseudopotential, one that is widely recognized currently for its broad utility. They also use the screening function of Vashishta and Singwi [22]. In separate calculations, with either a hard-sphere or an experimental structure factor, they have noted that the use of the experimental structure factor improves their results by  $8 \mu\Omega$  cm over the calculation employing hard spheres; their best calculation, however, is still 20% below our experimental value for  $\rho$  for  $\ell$ -Ge (see table 2). Their calculated value for  $S$  for  $\ell$ -Ge is relatively good ( $-2.2 \mu\text{V}^{\circ}\text{C}^{-1}$ , compared with an experimental value of about  $-0.3 \mu\text{V}^{\circ}\text{C}^{-1}$ ).

In order to understand better the limitations of this pseudopotential method, and to extend its application to  $\ell$ -Si, we have also calculated  $\rho$  for  $\ell$ -Ge (and for  $\ell$ -Si) using the BHS pseudopotential [21], the experimental structure factor of Waseda [23], and the screening function of Vashishta and Singwi [22]. (We did not pursue a thermopower calculation because of the sensitivity that we discovered in the calculation of  $\rho$  to the input parameters.) In the range of  $Q$  required for calculation of transport properties, the x-ray diffraction structure factor reported by Waseda [23] compares well with other work, including the recent x-ray data of Kita *et al* [1], and the neutron data of Gabathuler and Steeb



**Table 2.** Calculated values of  $\rho$  and  $S$  for  $\ell$ -Ge and  $\ell$ -Si near their respective melting temperatures. (The numbers in the sequence brackets identify references.)

Metal	$\rho_{exp}$ ( $\mu\Omega$ cm)	$\rho_{calc}$ ( $\mu\Omega$ cm)	$S_{exp}$ ( $\mu\text{V}^\circ\text{C}^{-1}$ )	$S_{calc}$ ( $\mu\text{V}^\circ\text{C}^{-1}$ )
Ge	66.8 [present]	41.2 [present]	-0.3 [present]	-2.2 [15]
		55 [15]		-3.3 [20]
		66.2 [18]		-6.4 [16]
		45.5 [20]		-1.4 [17]
		75.9 [16]		-3.2 [18]
		57.4 [17]		
Si	75.2 [present]	66.6 [present]	-2.1 [present]	-3.6 [18]
		57 [5]		-1.1 [17]
		69 [11]		-10.1 [16]
		67.3 [18]		[Ge $A(Q)$ ]
		46.3 [17]		
		180 [16] [Ge $A(Q)$ ]		

[19]. The BHS pseudopotential also includes relativistic effects on the valence electrons by the atomic core region. This treatment has been validated by close agreement between calculations [21] and experiment for such properties as bulk moduli and phonon frequencies. Si and Ge have been specifically noted as two elements well described by this formulation [21]. (Stich *et al* [5] and Kresse and Hafner [24] have also used BHS potentials in their calculations recently. These potentials were modified slightly to lessen the number of high-frequency components in the potential and to ease its use in LDF calculations, but these modifications appear mostly above  $Q = 2k_F$  and are outside the area of importance for calculation of transport properties by the Ziman formula.) For our purposes the non-local BHS pseudopotential should be fully adequate.

The value that we calculate for  $\rho$  for  $\ell$ -Si,  $66.6 \mu\Omega$  cm, is rather close to the experimental value, but the result for  $\ell$ -Ge is not nearly so good ( $41.2 \mu\Omega$  cm). We found that, if we used the screening function of Itchumaru and Utsumi (IU) [25] in this calculation, even though it differed rather little from that of Vashishta and Singwi, we obtained a value for  $\rho$  for  $\ell$ -Ge that was even lower by about  $15 \mu\Omega$  cm. (The small difference between the two screening functions occurs mainly in the range of  $Q$  where  $A(Q)$  is large and contributes substantially to the calculation of  $\rho$ .) The calculation of  $\rho$  for  $\ell$ -Si is affected much less by use of the IU screening function, lowering  $\rho$  by only  $4 \mu\Omega$  cm. Nonetheless, because of these sensitivities, we do not report calculations of thermopowers for these liquids.

It would now be especially interesting to see the results of applying the recently developed and highly successful *ab-initio* molecular dynamics methods of Car and Parrinello [7] to a calculation of the transport properties of  $\ell$ -Ge and  $\ell$ -Si. Some work along these lines has begun. As noted above, Stich *et al* [5] have successfully used optimally smooth BHS pseudopotentials to calculate numerous properties of  $\ell$ -Si, including the structure factor and DOS; additionally, an extrapolation of AC conductivity to the DC limit for  $\ell$ -Si gives a resistivity of  $57 \mu\Omega$  cm, in reasonable agreement with the measured value. Kresse and Hafner [6] have calculated the DOS for  $\ell$ -Ge with the same method and this is in very good agreement with experiment, although no estimate of resistivity was given. Now that good experimental data are available for  $\rho$  and  $S$  for  $\ell$ -Ge and  $\ell$ -Si, it would be especially interesting to apply these new methods to the calculation of these parameters.

## Acknowledgment

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