Temperature coefficient of the resistivity and thermopower of pure liquid germanium: a new approach

Temperature coefficient of the resistivity and thermopower of pure liquid germanium: a new approach

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Abstract.   We have recently published our experimental results on the resistivity (ρ) and on the absolute thermoelectric power (S) of liquid germanium. We complete the first paper by presenting improved theoretical calculations taking into account the generalized gradient approximation (GGA) with more recent exchange and correlation contributions. The principal purpose of this paper is to interpret the temperature dependence of the resistivity and of the thermopower of liquid germanium which are very sensitive physical properties. Earlier works have to our knowledge never treated rigorously the temperature dependence of the electronic transport properties. In the present paper we recalculate the muffin tin potential at each temperature using very accurate experimental pair correlation functions (available only for a few metals). We show that the increase in the atomic distance with the temperature rise changes the whole muffin tin potential and explains the temperature dependence of the electronic transport properties.

1. Introduction

The transition from the solid semi-conductor state to the metallic state at the melting point is accompanied by a volume contraction of about 5% [2]. The local order of the liquid germanium (6.8 nearest neighbours) is more compact than that of the crystalline state (four nearest neighbours) but less than normal liquid metals ($\approx$11 nearest neighbours). Due to the lack of an accurate experimental structure factor and pair correlation function, electronic transport properties are very often calculated using the hard sphere structure factor, which is very different from the experimental one for liquid germanium. Our 'ab initio' calculations [1] have been improved. We take into account a more recent expression of the exchange and correlation contribution proposed by Perdiew and Wang [3] (PW91) which has been used in this work simultaneously with another recent contribution of Perdiew, Burke and Ernzerhof [4] (PBE). We show that these contributions improve the calculated transport properties. The present paper is mainly devoted to discussing the temperature dependence of the resistivity and of the thermopower. When the temperature rises, the atomic volume changes. This is taken into account explicitly both in the prefactor of the resistivity and in the normalization term of the t matrix. A consequence is the modification of k_F and of E_F which also appears explicitly in the resistivity and in the thermopower formula. However, when the temperature rises, the distance between atoms increases. The construction of the muffin tin potential depends from the distances of the neighbours through the pair correlation function used in weighting the

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superposition of neighbouring potentials. Thus it is necessary, as the temperature is changed, to recalculate the muffin tin potential and the energy dependent phase shifts at *each temperature*. This needs the knowledge of an accurate (experimental or calculated) pair correlation function at each temperature. This calculation has never been done to our knowledge before. In section 2 we first recall very briefly the principal formula of the resistivity and thermopower. In section 3 we make explicit the modification to earlier calculations and present our new improved resistivity and thermopower calculations. Finally in section 4 we calculate and discuss the resistivity and thermopower temperature coefficients.

2. Theory

2.1. Expression of the resistivity and thermopower

We interpret the electrical resistivity of a normal metal as a function of the energy E and wavevector k following a scheme described by Makradi *et al* [1] using the Ziman [5] formula, which can be written:

$$\rho(E) = \frac{3\pi \, m_e^2 \Omega_0}{4e^2\hbar^3 k^6} \int_0^{2k} a(q)|t(q,E)|^2 q^3 \, \mathrm{d}q \tag{1}$$

where Ω_0 is the atomic volume, k and E are related by $E = \hbar^2 k^2/2m_e$ (following the approach of Esposito *et al*, which will be discussed in section 2.3), q is the transfer wavevector, $a(q)$ is the structure factor, $t(q, E)$ is the t matrix expressed in term of phase shifts [6, 7]

$$t(q,E) = -\frac{2\pi\hbar^3}{m\sqrt{2mE}\Omega_0} \sum_l (2l+1) \sin \eta_l(E) \, \exp(\mathrm{i}\eta_l(E)) P_l(\cos\theta) \tag{2}$$

where $P_l(\cos\theta)$ are the Legendre polynomials and θ is the angle between the incident and scattered wavevector. The phase shifts $\eta_l(E)$ are calculated from muffin tin potentials determined following the method of Mukhopadhyay *et al* [8]. Different exchange–correlation potentials, added to the electrostatic Coulomb part, were used in the construction of the muffin tin potential. If the energy-dependent phase shifts are known, this approach gives an energy-dependent resistivity and permits the calculation of the thermopower as follows:

$$S(E) = -\frac{\pi^2 k_B^2 T_K}{3|e|E} \chi \qquad \text{with } \chi = -\left[\frac{\partial \ln \rho(E)}{\partial \ln E}\right] \tag{3}$$

where k_B is the Boltzmann constant, T_K the absolute temperature in Kelvin and χ the dimensionless thermoelectric parameter. To compare to the experiment it is necessary for the resistivity, the thermopower and the thermoelectric parameter to take their values at E_F. The thermoelectric parameter can also be written: $\chi = 3 - 2\alpha - \beta/2$, where the expressions of α and β can be found in the paper of Vinckel *et al* [9].

2.2. Muffin tin potentials

The phase-shifts are calculated from muffin tin potentials. The construction procedure has been given by Mattheiss [10] for solids and has been adapted to (disordered) liquid metals by Mukhopadhyay *et al* [8]. The atomic environment is introduced by the experimental or theoretical pair correlation function $g(r)$ as described by Makradi *et al* [1]. The potentials used in this work derive from the density functional theory (DFT). The DFT [11, 12] is the basis of current research on the electronic properties of condensed matter [13] and is widely used in studies of molecules and other finite systems [14, 15]. During the last two decades [15] the local density approximation (LDA) has been used successfully to calculate the structural properties

of solids, including the stability, lattice constant, bulk moduli and phonon spectra. In the limit of slowly varying density, the homogeneous electron gas can replace the full electron system, and the LDA is a very good approximation. Makradi *et al* [1] show that this theory gives also good results for the liquid phase. The overestimation of binding energy of molecules or solids and the underestimation of the gap in insulators and bond lengths are well known deficiencies of the LDA that limit its further application [15]. The valence bandwidth narrowing in free-electron-like metal systems was not reproduced by using the LDA approach [16] because of inhomogeneous correlation effects. Recently these effects were discussed in the literature with simple recipes for correcting the LDA [17]. A generalized gradient approximation (GGA) for the exchange–correlation functional with explicit dependence on the gradient of charge density [18–21] in the DFT extends the practical implementation of DFT to inhomogeneous systems. Computationally it is simple to extend the LDA functional to a GGA non-local functional with simple calculations of the density. Calculations with:

- the functional of Perdiew and Wang (PW86) [19],
- Becke's exchange [21] plus Perdiew's correction (BP) [20],
- the recent functional of Perdiew and Wang (PW91) [3],

have been tested [22]. The superiority of the GGA with respect to the LDA is not clear when it is applied to solids. Sometimes the GGA reproduces well the experimental phenomena; in other cases the GGA overcorrects the LDA results. In this paper we also consider the simplified version of the GGA functional by Perdiew *et al* [4] (PBE) which satisfies many exact properties of DFT. The indicated major improvements over PW91 are the accurate description of the linear response of the uniform electron gas, proper uniform scaling and smoother potentials [4].

2.3. Fermi energy

To determine the resistivity and thermopower at the Fermi energy different methods have been discussed in [1]. The Fermi energy calculation used in this work was that proposed by Esposito *et al* [23]. The position of E_F, with respect to the scattering muffin tin zero potential, depends on the shape of the density of states $N(E)$ which has been determined following Lloyd's [24] method. Esposito *et al* [23] introduced the number of conduction electrons per atom N_C (effective valence) which is different from the valence Z. The Fermi energy is obtained by filling the density of state curve by Z electrons per atom. The Fermi wavevector k_F is obtained from E_F; N_C is obtained from k_F. All details can be found in [1].

3. Resistivity and thermopower as function of energy

New calculated resistivities and thermopowers are obtained with the simple LDA and the two GGA corrections proposed by Perdiew *et al* [3, 4]. In this calculation, the first and second gradient of the electronic density, which appears in the GGA approximation of the correlation–exchange potential, are calculated self-consistently. At each iteration, after solving the Schroedinger equation we calculate the (first and second) gradient of the corresponding electronic density. This density will be introduced in the correlation–exchange potential used in the following iteration. In the earlier calculations of Makradi *et al* [1] the electronic density has been calculated by using the Clementi [25] partial wave functions.

In this section, the calculations are made using only the very accurate experimental structure factor given by Bellissent-Funel and Bellisent [26] measured with a 640-cell neutron multidetector. In figure 1 we present the energy dependence of the resistivity calculated with the different exchange–correlation potentials. The general behaviour of all curves is the
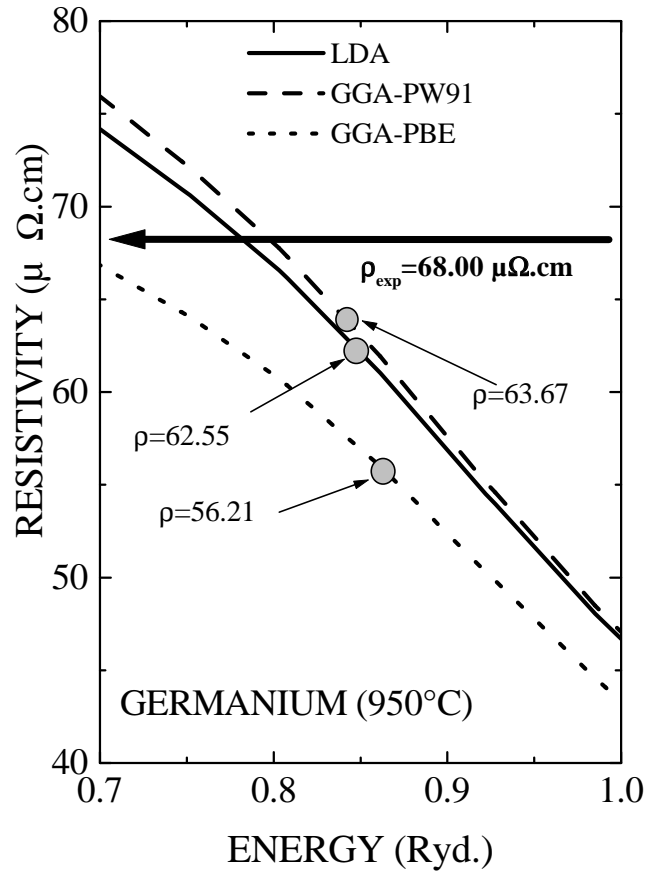
Figure 1. Energy dependence of the electrical resistivity of liquid germanium. Calculations were made at 950 °C using the local density approximation (LDA) and the generalized gradient approximation of Perdiew and Wang (GGA-PW91) and Perdiew, Burke and Ernzerhof (GGA-PBE).

same as those of Makradi *et al* [1]‡, thus in figure 1 we show just the part around the Fermi energy. The present calculations give better results for the resistivity; all curves move at higher resistivities than our earlier calculations. The values at E_F are reported in table 1. The GGAs are introduced by the PW91 and PBE exchange–correlation approximations to consider the inhomogeneity of the electronic density.

The GGA-PW91 calculation gives the best result with 63.67 $\mu\Omega$ cm at 0.8416 Rydberg while the GGA-PBE approximation gives 56.21 $\mu\Omega$ cm. GGA-PW91 is very close to the experimental result of 67.97 $\mu\Omega$ cm. The LDA value of 62.55 $\mu\Omega$ cm is between the two GGA approximations. The superiority of GGA with respect to LDA is not as clear for the liquid (germanium) state as for solids.

Considering the thermopower, the calculated values obtained with all the approximations of the density functional theory are very close to Makradi's values [1]. The differences between them are very small and do not exceed 0.05 μV K^{-1}. The average value is about -1.86 μV K^{-1}. The curves have the same behaviour than those of [1]; thus we represent in figure 2 the values of the thermopower on an expanded scale near the Fermi energy. The calculated thermopowers are

‡ A small error in LDA calculation has been corrected in the present work.

Table 1. Fermi energy E_F, effective number of conduction electrons N_C, resistivity $\rho(E_F)$ and thermopower $S(E_F)$ of liquid germanium. Calculations were made with the DFT approach for different correlation and exchange terms (LDA, GGA-PW91 and GGA-PBE).

Germanium 950 °C	E_F (Rydberg)	N_C	$\rho(E_F)$ ($\mu\Omega$ cm)	$S(E_F)$ (μV K^{-1})
LDA	0.8451	3.894	62.55	−1.85
GGA-PW91	0.8416	3.870	63.67	−1.89
GGA-PBE	0.8588	3.989	56.21	−1.84
Experimental resistivity ($\mu\Omega$ cm)			67.98 ± 0.30 [1]	
Experimental thermopower (μV K^{-1})				−0.23 ± 0.40 [1]

less than 1.5 μV K^{-1} from the experimental values which can be considered as very good (for the thermoelectric power which takes positive or negative values, the accuracy of measurements and calculations has to be compared in absolute terms and not as a percentage). All calculations underestimate the experimental thermopower and the differences are not significant. In this case we cannot say that the superiority of GGA is clearly demonstrated for thermopower calculations of liquid germanium.

4. Temperature dependence

4.1. General considerations

The different contributions for the temperature dependence of the electronic transport properties have been taken into account by several authors [5, 27–29]. A quantitative theoretical discussion of the temperature coefficient was first given by Dreirach *et al* [6]. In their recent paper Rhazi *et al* [30] discussed qualitatively the effect of the temperature on each factor in the Ziman formula. In the present work we use an *ab initio* method by calculating the scattering of electrons (phase shifts) by muffin tin potentials. Nobody to our knowledge has discussed the temperature dependence by reconstructing the muffin tin potential at each temperature. It is the aim of this paper to do it. This calculation is possible for liquid germanium which is one of the scarce liquid metals for which accurate pair correlation functions have been determined at different temperatures.

The important success of Ziman [5] was that his theory could explain roughly and qualitatively the electronic transport properties of alkaline metals (Ziman [5]), of polyvalent metals (Bradley *et al* [27]) and of normal metallic alloys (Faber and Ziman [28]) using the pseudopotential theory. Noble metals (Evans *et al* [29]) and alloys of noble and transition metals (Dreirach *et al* [6]) were treated with the *t* matrix approach. Ziman's theory explains qualitatively the decrease of the resistivity with temperature for liquid zinc and for binary alloys at the mean valence of 1.8. The explanation comes from the temperature dependence of the structure factor near the main peak. This main peak region is heavily weighted by a q^3 factor because the limit of integration $2k_F$ is near the maximum of the first peak of the structure factor for the mean valency of 1.8. Nevertheless the temperature dependence which is very sensitive to the theoretical model was not well treated from a quantitative point of view. Ziman [31], in his review article at the first liquid metal conference, compared the experimental temperature coefficient at constant pressure to a calculated one at constant volume. He discussed a reduced
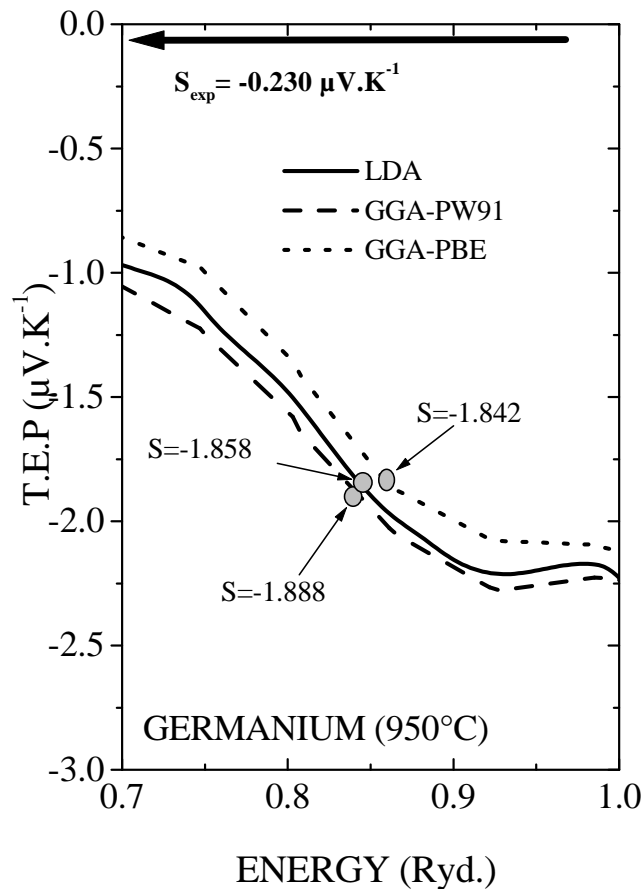
Figure 2. Energy dependence of the thermopower of liquid germanium. Calculations were made at 950 °C using the local density approximation (LDA) and the generalized gradient approximation of Perdiew and Wang (GGA-PW91) and Perdiew, Burke and Ernzerhof (GGA-PBE).

temperature coefficient introduced by Greenfield and explains that the good agreement with the experiment in the reduced temperature coefficient is not fortuitous because the effect due to the expansion is compensated. The temperature coefficient of the thermopower was not discussed in his paper. Waseda and Suzuki [32] determined the experimental structure factor of liquid mercury and obtained good results with the pseudopotential of Evans [33]. Evans [34] determined the temperature dependence of the resistivity and thermopower for some polyvalent metals (In, Cd, Te, Pb and Hg). He takes into account the experimental structure factor, the change in the atomic volume and its influence on the dielectric screening function, but he assumes that the bare potential of the ion does not change with density. Minoo *et al* [35] proposed a simple phenomenological structure factor $a(q)$ for liquid alkali metals and used it to calculate the temperature coefficient of the resistivity at constant volume. The form factor was obtained in the framework of the empty-core model [36], the empty-core R_C radius was adjusted to reproduce the experimental resistivity at melting. Bellissent-Funel *et al* [37] determined very accurately the experimental structure factor of liquid gallium between 303 and 573 K. They fit the unique Ashcroft [38] parameter R_C on the experimental resistivity using the Ziman formula. They showed that R_C, thus the bare potential, was temperature dependent.

More recently Sarita *et al* [39] determined the temperature dependence of the electronic transport properties. They took into account the temperature dependence of the structure factor, which was determined theoretically on the basis of the knowledge of the experimental structure factor at one temperature. For this it is necessary to use the 'Debye temperature' treated as a parameter. The form factor was determined by a 'first principles' calculation with the non-local optimized Shaw [40] model potential theory. As pointed out by Sarita *et al*, most (all?) authors considered that the pseudopotential matrix elements remain unchanged on thermal expansion. Sarita *et al* determined the form factor by taking into account the atomic volume and k_F appropriate to the temperature of investigation, but did not, as far we understand, recalculate the absolute Fermi energy in order to determine the parameters $A_l(E_F)$ at each temperature. In the Shaw model potential theory the parameters are calculated as a function of energy relatively to an absolute energy scale (the energy to put an electron at infinity). This energy is always obtained following a method derived from Animalu and Heine [41]. It is necessary to introduce especially the mean ionization energy, the binding energy per valence electron, the exchange and correlation energy of the free electron gas. Ballentine and Gupta [42], Ese and Reissland [43] and Cowley [44] have developed different methods of calculating the Fermi energy, but nobody to our knowledge determined the absolute Fermi energy as a function of temperature.

Our approach is different but follows the same philosophy, i.e. it is necessary to determine at each temperature the energy dependent parameters, which describe the scattering. In our approach we use the *t* matrix expression as a function of energy dependent phase shifts at the place of pseudopotential form factors with energy dependent parameters. However the energy is not related to the same origin. In the *t* matrix formulation the zero of energy is the muffin tin zero potential. When the electron energy is lower than the muffin tin potential, the electron cannot jump the potential barrier. When it is above the electron is scattered. The Fermi energy is determined following the method described by Makradi *et al* [1]. It can be obtained as a function of temperature more easily than in the pseudopotential approach. This is the aim of the present work.

In the Ziman expression of the resistivity (formula (1)) and of the thermopower (formula (3)) different temperature dependent parameters appear. The most important is the atomic volume Ω_0 determined from the mass density of the metal. We used the Crawley [45] expression of the density, which is given as a linear function of the temperature. The wavevector k that appears in the prefactor and in the upper integral limit is directly expressed as a function of the atomic volume Ω_0. The energy is expressed as a function of the wavevector. The energy and the atomic volume appear explicitly in the *t* matrix expression (formula (2)). The thermopower is proportional to the temperature and to the thermoelectric parameter χ and inversely proportional to the energy. The thermoelectric parameter χ is expressed as a function of the resistivity integral (term α) and of an integral, in which appears the derivative of the *t* matrix with regard to E (term β) [9].

It is relatively easy to take into account the temperature dependence of the mass density, thus the atomic volume, thus the wavevector, thus the energy, thus the *t* matrix. The structure factor can also be calculated as a function of temperature. For example the hard sphere structure factor depends on the density (given by Crawley) and on the packing fraction (given by Waseda). One can also use, if available, the experimental structure factor at two temperatures. Such a kind of calculation has even been done before. However the phase shifts have always been determined at one temperature only and have been used at another one. Sometimes the phase shifts have been determined as a function of energy. It is then possible to use the phase shifts at the energy corresponding to the temperature. Such calculations have even been done in earlier works of our laboratory.
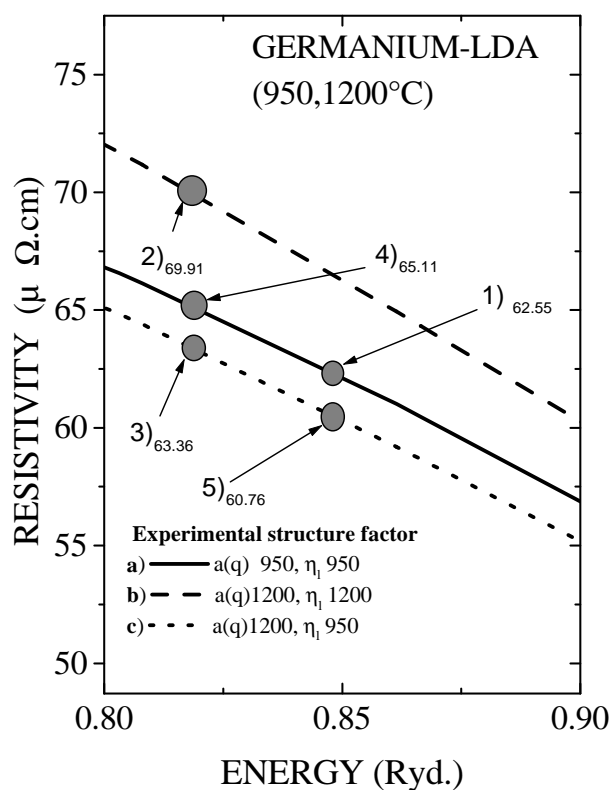
Figure 3. Energy dependence of the electrical resistivity of liquid germanium at 950 and 1200 °C with the experimental structure factor and pair correlation function. Calculations were made using the local density approximation (LDA). Curve a is constructed using the experimental structure factor at 950 °C; the muffin tin potential is constructed from the experimental pair correlation function at 950 °C. Curve b is constructed using the experimental structure factor at 1200 °C; the muffin tin potential is constructed from the experimental pair correlation function at 1200 °C. Curve c is constructed using the experimental structure factor at 1200 °C, but the muffin tin potential (hence the energy dependent phase shifts) is the same that at 950 °C.

However there is an important temperature contribution which has never been studied before to our knowledge. Indeed, when the temperature rises, the liquid metal expands and the whole muffin tin potential is modified because of the superposition of the neighbouring atomic potentials, the distance between them being greater. This has an important influence on the phase shifts versus energy curves, thus on the resistivity and thermopower versus energy curves. Such calculations are possible, but very precise experimental pair correlation functions at different temperature are scarce. In the case of liquid germanium, Bellisent-Funel and Bellissent [26] have calculated pair correlation functions by a Fourier transform of their accurate structure factors measured over a wide q range at two temperatures. They provide us with their experimental data. We use their experimental $a(q)$ to determine the resistivity and thermopower versus energy at two temperatures.

4.2. Resistivity coefficients

In figure 3 we represent on an expanded scale three resistivity versus energy curves calculated using the experimental structure factor in the Ziman formula and the experimental pair
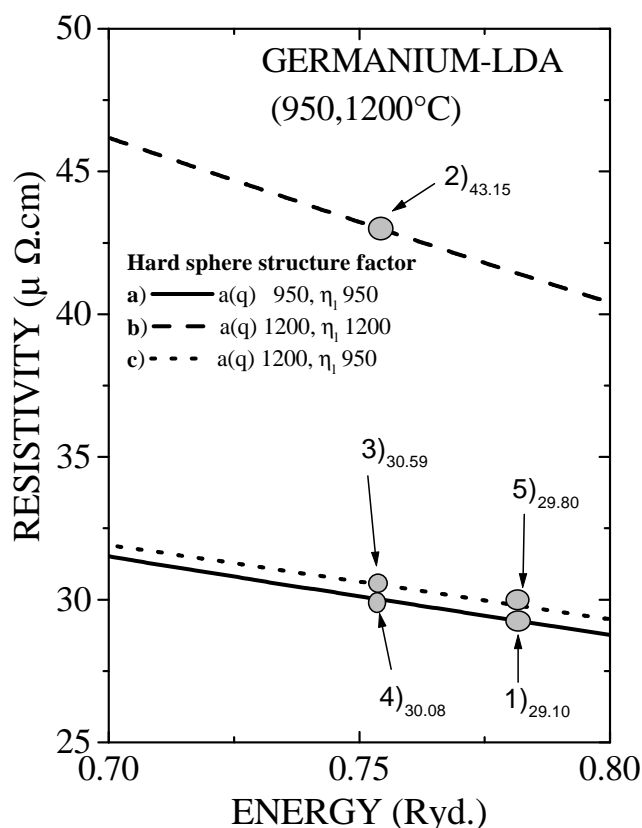
Figure 4. Energy dependence of the electrical resistivity of liquid germanium at 950 and 1200 °C with the hard sphere structure factor and pair correlation function. Calculations were made using the local density approximation (LDA). Curve a is constructed using the hard sphere structure factor at 950 °C; the muffin tin potential is constructed from the hard sphere pair correlation function at 950 °C. Curve b is constructed using the hard sphere structure factor at 1200 °C; the muffin tin potential is constructed from the hard sphere pair correlation function at 1200 °C. Curve c is constructed using the hard sphere structure factor at 1200 °C, but the muffin tin potential (hence the energy dependent phase shifts) is the same that at 950 °C.

correlation function $g(r)$ (Waseda) in the muffin tin potential construction. The first curve is obtained by determining the phase shifts using the $g(r)$ at 950 °C. Evidently the resistivity $\rho(E)$ is calculated using the structure factor at the same temperature. The resistivity at 950 °C is represented by point 1 indicated on the curve a) $a(q)$ 950 °C, η_l 950 °C (which means that the structure factor $a(q)$ is taken at 950 °C in Ziman's formula and that the phase shifts η_l have been constructed using the experimental pair correlation function $g(r)$ measured at 950 °C). Its value is 62.55 $\mu\Omega$ cm. The first approximation is to take only into account the change in density, wavevector and energy; we obtain point 4 on the same curve a). The resistivity is 65.11 $\mu\Omega$ cm. The temperature coefficient is 10.22 nΩ cm K^{-1} to be compared to our experimental value of 16.6 nΩ cm K^{-1}. Another inexact approximation consists of taking into account only the structure factor change and not the effect of the density, and of k_F and E_F. We obtain point 5 with a resistivity of 60.76 $\mu\Omega$ cm on the curve c) $a(q)$ 1200 °C, η_l 950 °C. The resistivity temperature coefficient is now -7.2 nΩ cm K^{-1} which is negative. To increase the correctness of the calculation, we can use in the Ziman formula the experimental
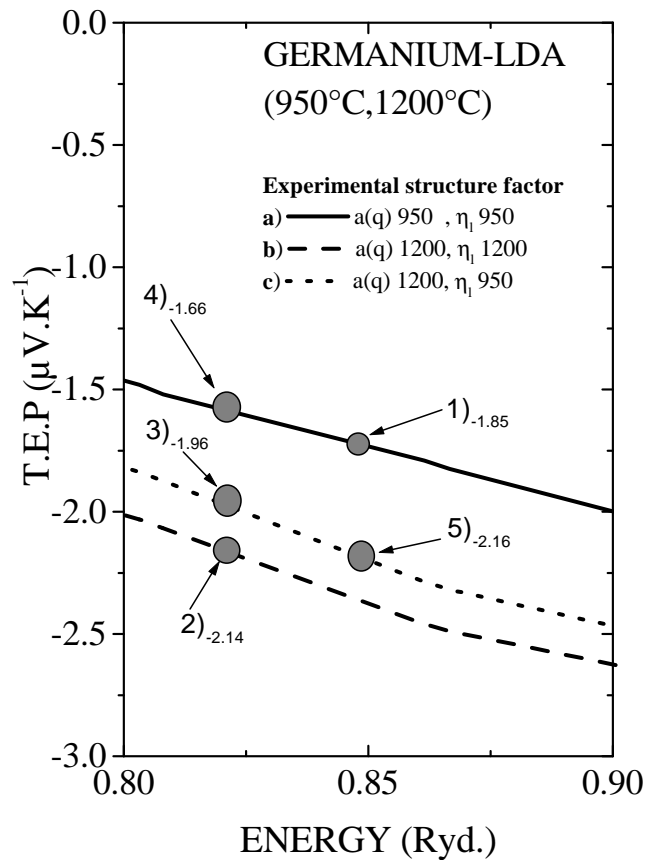
Figure 5. Energy dependence of the thermopower of liquid germanium at 950 and 1200 °C with the experimental structure factor and pair correlation function. Calculations were made using the local density approximation (LDA). Curve a is constructed using the experimental structure factor at 950 °C; the muffin tin potential is constructed from the experimental pair correlation function at 950 °C. Curve b is constructed using the experimental structure factor at 1200 °C; the muffin tin potential is constructed from the experimental pair correlation function at 1200 °C. Curve c is constructed using the experimental structure factor at 1200 °C, but the muffin tin potential (hence the energy dependent phase shifts) is the same that at 950 °C.

structure factor at the temperature of 1200 °C and the change in Ω_0, k_F and E_F. The resistivity is 63.36 $\mu\Omega$ cm and is represented by point 3 on the curve indicated c) $a(q)$ 1200 °C, η_l 950 °C. The temperature coefficient of the resistivity is now 3.2 nΩ cm K^{-1} with a theoretically more exact approach.

These results show clearly that contrary to what has been written in older papers the structure factor effect is not the predominant contribution and that the change in k_F resulting from the density is more important than the structural effect. Finally we recalculate the phase shifts at a different temperature. This gives us the curve indicated b) $a(q)$ 1200 °C, η_l 1200 °C. The resistivity at the Fermi energy is 69.91 $\mu\Omega$ cm and is represented by point 2 on the curve b). The temperature coefficient is now 29.4 nΩ cm K^{-1}. It is clear from these results that to compare experience and theory it is absolutely necessary to recalculate the phase shifts at each temperature. Of course the calculated value is not fully satisfactory, the result with point 4 is nearer the experimental value, but it has been obtained with a wrong method of

Table 2. Different temperature coefficient of the resistivity and of the thermopower. Points 1, 2, 3, 4 and 5 have the same meaning as in figures 3, 4, 5 and 6.

Germanium 950 °C	$\left(\dfrac{\partial \rho}{\partial T}\right)$ Experimental structure factor in nΩ cm K^{-1}	$\left(\dfrac{\partial \rho}{\partial T}\right)$ Hard sphere structure factor in nΩ cm K^{-1}	$\left(\dfrac{\partial S}{\partial T}\right)$ Experimental structure factor in nV K^{-2}	$\left(\dfrac{\partial S}{\partial T}\right)$ Hard sphere structure factor in nV K^{-2}
Calculation with atomic volume dependence (points 1 and 4)	10.2	3.9	0.77	−0.09
Calculation with structure factor dependence (points 1 and 5)	−7.2	2.8	−1.24	−1.00
Calculation with atomic volume and structure factor dependence (points 1 and 3)	3.2	6.0	−0.41	−0.63
Complete calculation (points 1 and 2)	29.4	56.2	−1.16	−5.59
Experimental resistivity temperature coefficient	16.6 [1]	16.6 [1]		
Experimental thermopower temperature coefficient			−0.83 [1]	−0.83 [1]

calculation. This put serious doubt on earlier results, which sometimes are fortuitously near the experimental value.

The lack of experimental structure factors has often led physicists to make calculations with theoretical structure factors like the hard sphere structure factors. However it is necessary to use a temperature dependent hard sphere diameter σ. Gasser *et al* [46] have discussed the temperature dependence of the hard sphere diameter. In the present work we used the germanium hard sphere structure factor given by Waseda at 950 °C and extended by 1200 °C by the Protopapas [47] formula. We do not discuss the resulting electronic transport properties. The reader can find all the quantitative information in figure 4 and in table 2. It is clear that the hard sphere structure factors cannot be used for liquid germanium.

4.3. Thermoelectric power coefficients

We present in figure 5 the thermoelectric power as a function of energy on a very expanded scale calculated with the experimental structure factor and correlation pair function. Here again we can calculate the temperature dependence by making several assumptions.

The thermopower is determined with a unique set of phase shifts versus energy:

- we take into account the volume dependence alone (points 1 and 4 on curve a)),
- we take into account the structure factor alone (points 1 and 5 on curve c)),
- we take into account both the volume and structure factor dependence (points 1 and 3 on curve c)),
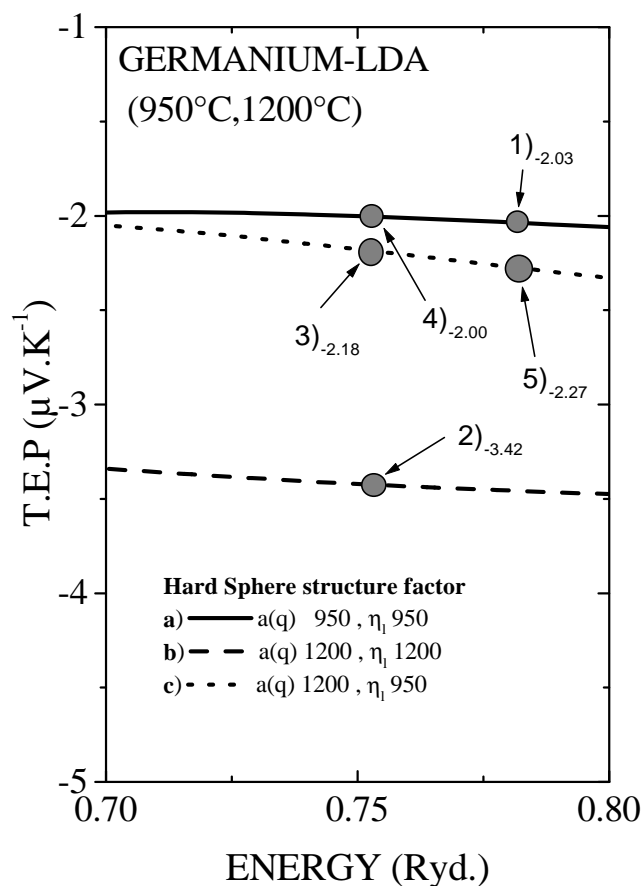
Figure 6. Energy dependence of the thermopower of liquid germanium at 950 and 1200 °C with the hard sphere structure factor and pair correlation function. Calculations were made using the local density approximation (LDA). Curve a is constructed using the hard sphere structure factor at 950 °C; the muffin tin potential is constructed from the hard sphere pair correlation function at 950 °C. Curve b is constructed using the hard sphere structure factor at 1200 °C; the muffin tin potential is constructed from the hard sphere pair correlation function at 1200 °C. Curve c is constructed using the hard sphere structure factor at 1200 °C, but the muffin tin potential (hence the energy dependent phase shifts) is the same that at 950 °C.

- the thermopower is determined with a temperature dependence of the volume, of the structure factor and the phase shifts are calculated at each temperature (points 1 and 2 on curve b)).

We can here consider in table 2 that the best approach *gives also the best result*.

As for the resistivity the calculations have also been made with hard sphere structure factors. All results are reported in figure 6 and table 2. It is clear that for hard sphere the best theoretical calculation gives a very bad result and that fortuitously an inexact calculation gives reasonable results. The hard sphere model does not describe satisfactorily the electronic transport properties.

5. Conclusion

Until now, the temperature coefficients of the transport properties have been calculated by making different approximations:

- temperature dependent atomic volume (hence temperature dependent k_F and E_F),
- temperature dependent structure factor,
- temperature dependent atomic volume and structure factor.

In the present work we add a new set of phase shifts derived from a *muffin tin potential reconstructed at each temperature*. It is clear from table 2 that this effect is very important and can no longer be neglected for every temperature dependent property. With this method we can see that the hard sphere structure factor does not allow us to construct a realistic muffin tin potential for liquid germanium. The complete calculation overestimates the temperature coefficient of the resistivity while the temperature coefficient of the thermopower can be considered as well described by this new approach. It is now clear that an accurate calculation of the temperature coefficient needs an accurate experimental pair correlation function and that this new contribution to the temperature coefficient of the resistivity is quantitatively as important, if not more, than the volume dependence or (and) the structure factor dependence.

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