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1990 J. Phys.: Condens. Matter 2 2297

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# Electronic properties of liquid metals and alloys calculated with the first-principles model (pseudo)potential of Bachelet, Hamann and Schlüter: the Ga–Ge system

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Received 30 May 1989, in final form 13 September 1989

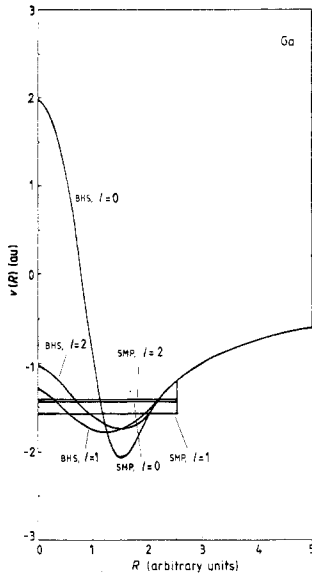
**Abstract.** A model (pseudo)potential method has proven to be an interesting technique for calculating electronic properties in the framework of the Ziman formula for pure liquid metals and the Faber–Ziman expression for liquid alloys. First-principles model potentials are non-local and their parameters are energy dependent. In the alloy one must take into account an energy dependent effective mass, a depletion hole and the Fermi energy core shift which is not known for alloys. Furthermore, the thermopower explicitly includes an energy dependent contribution. The first-principles model (pseudo)potential of Bachelet, Hamann and Schlüter (BHS) is energy independent and avoids the necessity of making these corrections. It has been used to calculate analytically the corresponding form factor. The resistivity and the thermopower of pure germanium and gallium and of the germanium–gallium alloy have been determined by using the Faber–Ziman formalism. Both hard sphere and experimental structure factors have been used (when available). The agreement between experimental and theoretical properties can be considered as good and confirms that the BHS model potential is adequate for describing the electronic properties of liquid alloys.

## 1. Introduction

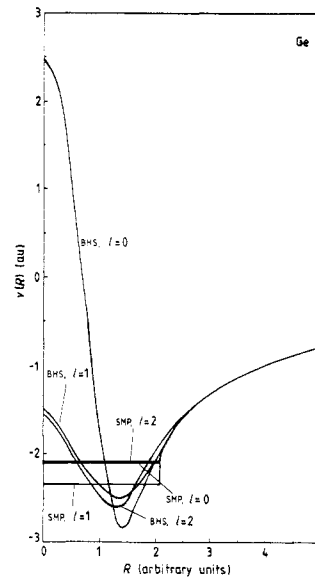
A pseudopotential method has proven to be an interesting and useful technique for calculating electronic properties of liquid metals [1] and alloys [2] in terms of pseudopotential form factors and structure factors. Recently, Bachelet, Hamann and Schlüter (BHS) [3] introduced a new family of pseudopotentials. The aim of this work is to compute with it the ‘on-Fermi-sphere’ form factor, and different properties like the resistivity and thermoelectric power of liquid metals and alloys.

The basic starting point for investigating these properties is the pseudopotential form factor which is the matrix element of the pseudopotential between plane waves. The pseudopotential theory consists of replacing the deep core potential at each ionic site by a weak pseudopotential (and the corresponding wave function by a pseudowave one). The latter is constructed to preserve the eigenvalues of the Schrödinger equation.

Two approaches have been used. The first one is the model (pseudo)potential method. It is a ‘first-principles’ theory in the sense that the parameters of the model potential are fitted to atomic spectroscopic experimental data. This theory has been



**Figure 1.** Pseudopotentials of Ga for each value of the angular momentum  $l$ , from BHS [3] and SMP [8] models.



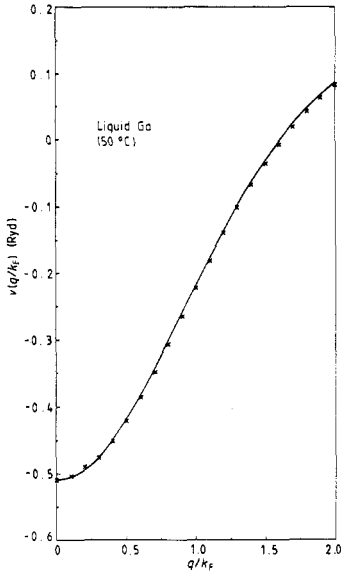
**Figure 2.** Pseudopotentials of Ge for each value of the angular momentum  $l$ , from BHS [3] and SMP [8] models.

developed by, among others, Heine, Abarenkov, Animalu, Shaw, Harrison, So, Moore and Wang [4–11]. The price to pay for the simplification of the theory consists in introducing the non-locality of the model potential and letting the parameters be energy dependent.

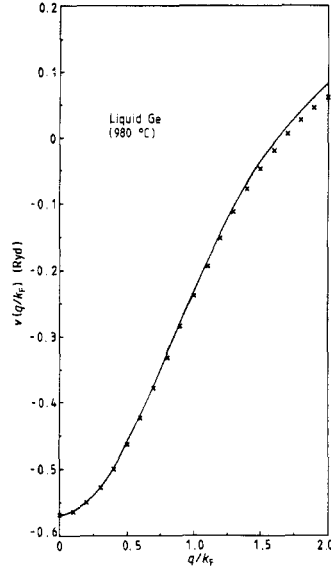
The second approach is that of pseudopotentials obtained by the orthogonalisation of wave functions to core states (OPW method). It has been developed by Austin, Heine, Sham and Weaire [12–14], and for liquid metals by Hafner [15]. This procedure is an *ab initio* method.

First-principles model potentials are non-local and their parameters are energy dependent. In the alloy one must take into account an energy dependent effective mass, a depletion hole and the Fermi energy core shift which is not known for alloys. Recently BHS [3] introduced a new family of energy independent models of pseudopotentials which avoid the necessity of making these corrections. They have many interesting properties—e.g. they are transferable and they can be fitted with simple continuous analytic functions on their *ab initio* pseudopotentials. Furthermore, BHS claim that their model potential has been developed for the entire periodic table (from hydrogen to plutonium). This includes the noble, the transition and the rare earth metals which are not well described by the Heine–Abarenkov–Animalu–Shaw model potential family. In figures 1 and 2 we have represented the model potential of BHS [3] and have compared it to that of Animalu and Heine [6] for gallium and germanium respectively. The energy independence of the parameters of the BHS potential allows the ‘transfer’ of these values to the alloy case. However, the model potential ‘on-Fermi-sphere’ form factors, and the electronic properties of liquid metals and alloys derived from the model potential of BHS [3] have not yet been calculated as far as we know.

The purpose of this work is to present the resistivity and the absolute thermoelectric power of liquid gallium, germanium and of gallium–germanium alloys, which have been computed in the framework of the Faber–Ziman formula. In our calculations we have



**Figure 3.** Pseudopotential form factors of Ga as a function of the momentum transfer  $q$ . Full curve: BHS [3, 16]; crosses: SMP [8].



**Figure 4.** Pseudopotential form factors of Ge as a function of the momentum transfer  $q$ . Full curve: BHS [3, 16]; crosses: SMP [8].

used the locally screened form factor (figures 3 and 4) which we have calculated analytically from the BHS pseudopotential [16]. The results are compared with the Animalu [8] simple model potential (SMP) form factor.

## 2. Formalism

### 2.1. Electrical resistivity

According to the Ziman formula [1], the electrical resistivity of a pure liquid metal can be written as

$$\rho = \frac{3\pi m^2 \Omega_0}{4e^2 \hbar^3 k_F^6} \int_0^{2k_F} a(q)v(q)^2 q^3 dq. \tag{1}$$

We can see that the resistivity depends on two basic quantities, the pseudopotential form factor on the Fermi surface  $v(q)$  which is screened by the conduction electrons, and the liquid structure factor  $a(q)$ . This formula can be adapted to liquid alloys (Faber–Ziman [2]) by introducing partial structure factors [17] and form factors for each species  $i$  in the alloy.

### 2.2. Thermoelectric power

The absolute thermoelectric power is proportional to the logarithmic derivative of  $\rho$  with respect to  $k$  at  $k_F$ . In terms of Ziman’s formula [1] it takes the following form:

$$S = \pi^2 k_B^2 T \chi / 3eE_F \tag{2}$$

where  $\chi$  is the thermoelectric parameter which is given by

$$\chi = (k_F/2\rho)(\partial\rho/\partial k)_{k=k_F}. \tag{3}$$

**Table 1.** Least squares analysis of the electrical resistivity and thermoelectric power of liquid gallium and germanium. The correlation coefficient  $r$  is also given.

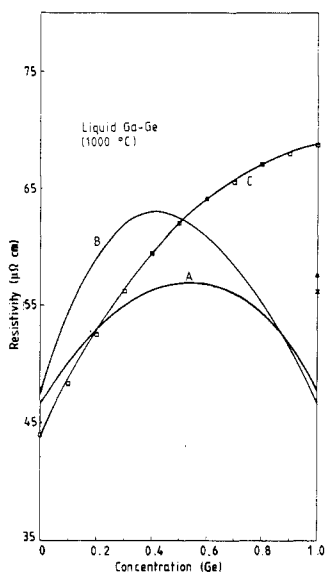
Resistivity of liquid gallium		
Experimental [22]	$\rho = 25.630 + 1.8360 \times 10^{-2} T_c$	$r = 1.000$
Calculated (BHS)	$\rho = 33.495 + 1.3874 \times 10^{-2} T_c$	$r = 0.999$
Calculated (SMP)	$\rho = 31.854 + 1.6205 \times 10^{-2} T_c$	$r = 0.999$
Resistivity of liquid germanium		
Experimental [23]	$\rho = 64.981 - 7.1196 \times 10^{-3} T_c + 1.0799 \times 10^{-5} T_c^2$ or $\rho = 53.227 + 1.5466 \times 10^{-2} T_c$	$r = 1.000$
Calculated (BHS)	$\rho = 31.845 + 1.6207 \times 10^{-2} T_c$	$r = 1.000$
Calculated (SMP)	$\rho = 30.626 + 1.6358 \times 10^{-2} T_c$	$r = 1.000$
Thermoelectric power of liquid gallium		
Experimental [22]	$S = -0.1897 - 1.7642 \times 10^{-3} T_c$	$r = 0.987$
Calculated (BHS)	$S = 0.42151 + 1.2651 \times 10^{-3} T_c - 1.1025 \times 10^{-6} T_c^2 - 1.1313 \times 10^{-9} T_c^3$	$r = 1.000$
Calculated (SMP)	$S = 0.21417 + 4.3509 \times 10^{-4} T_c - 1.0708 \times 10^{-6} T_c^2 - 8.6697 \times 10^{-10} T_c^3$	$r = 1.000$
Thermoelectric power of liquid germanium		
Experimental [24]	$S = 3.40 - 4.00 \times 10^{-3} T_c$	
Calculated (BHS)	$S = 0.88641 - 3.3437 \times 10^{-3} T_c$	$r = 0.999$
Calculated (SMP)	$S = 0.0321 - 4.5543 \times 10^{-3} T_c$	$r = 1.000$

### 3. Results and discussion

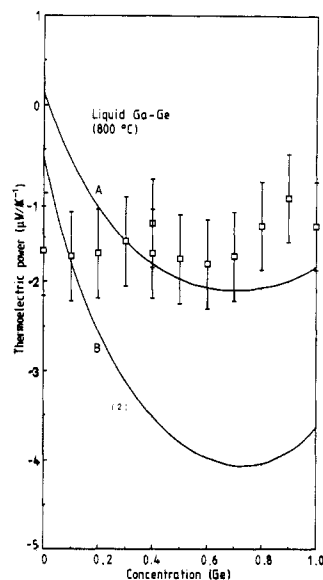
#### 3.1. Electrical resistivity

We have evaluated the resistivity of liquid germanium, gallium and germanium–gallium alloys at different temperatures with BHS [3, 16] and with SMP [8] model potential form factors. The bare BHS form factor (see figures 3 and 4) has been screened locally in the same manner as the SMP [8] one by the dielectric function of Vashishta and Singwi [18]. Our calculations have been performed with Ashcroft–Lekner [19] hard sphere structure factors for pure metals, and Ashcroft–Langreth [20] hard sphere partial structure factors for alloys. The hard sphere diameters have been chosen in the same manner as that described in an earlier paper [21]. In the alloy we have taken into account the modification of the mean atomic volume  $\Omega_0(T)$  and of the Fermi wavevector  $k_F$  by introducing  $Z(c)$  the mean valence and  $\Omega_0(T, c)$  the mean atomic volume of the alloy (obtained by a linear interpolation of the pure metal values [21]).

In table 1 we compare our results to the Anno [22] and Gasser [23] experimental values for pure metals. The resistivities computed with the BHS model pseudopotential are close to those computed with the SMP model (differing by less than  $1.5 \mu\Omega \text{ cm}$  for gallium, and  $1.1 \mu\Omega \text{ cm}$  for germanium), but the two models underestimate the resistivity of liquid germanium by about  $20 \mu\Omega \text{ cm}$ , and overestimate the resistivity of liquid gallium by about  $3 \mu\Omega \text{ cm}$ . However, the results depend sensitively on the experimental structure factors of Ga and Ge, which both present a shoulder on the high angle side of their first peak. We can observe that, with the experimental structure factors, we improve the resistivity by  $8 \mu\Omega \text{ cm}$  for germanium and  $2 \mu\Omega \text{ cm}$  for gallium.



**Figure 5.** Electrical resistivity of Ga-Ge at 1000 °C. Curve A: BHS [3, 16]; curve B: SMP [8]; curve C: experiment [22]. Triangle: BHS with experimental structure factor; cross: SMP with experimental structure factor.



**Figure 6.** Thermoelectric power of Ga-Ge at 800 °C. Curve A: BHS [3, 16]; curve B: SMP [8]; squares: experiment [25].

We have computed the resistivity of the Ga-Ge alloy at 1000 °C. Our results with BHS [3] and SMP [8] form factors are compared with the experimental resistivity. Figure 5 shows that our results are slightly different from those measured by Anno [22]. In the case of alloys, the partial experimental structure factors are not known. However, with hard spheres, the agreement with experimental data is satisfactory but could probably be improved with experimental structure factors.

### 3.2. Thermoelectric power

The absolute thermoelectric power has been computed for pure gallium and germanium and for the Ga-Ge system at 800 °C with the SMP (neglecting the energy dependent contribution) and BHS pseudopotentials. We have given our results for pure gallium and for pure germanium in table 1 with both model potentials. We compare our values to the experimental results obtained by Anno [22] for gallium (table 1). Both form factors give results very near to the experimental thermopower (differing by less than  $1.5 \mu\text{V K}^{-1}$ ). The calculated values presented a convex curve which could not be confirmed experimentally because the experimental accuracy was insufficient. We compare our values with the experimental results obtained by Bath [24] for germanium (table 1). The results obtained with BHS form factors are close to the experimental thermopower (within  $2.0 \mu\text{V K}^{-1}$ ). The results are better than for the SMP form factors which give results differing by  $4.5 \mu\text{V K}^{-1}$ . This is probably due to the neglected energy dependent contribution which does not appear in the BHS form factor. The influence of the experimental structure factor on the thermopower is very small (less than  $0.2 \mu\text{V K}^{-1}$ ). For the alloy, we compare our values with the experimental results obtained by Mayoufi [25] (figure 6). The divergence between the three curves is not very important since the scale is very expanded.

#### 4. Conclusions

BHS locally screened model (pseudo)potentials were used to compute the resistivity and the thermoelectric power of gallium, germanium and of the Ga–Ge system. We have compared our results with those obtained in another theoretical analysis (SMP locally screened model potential) and with experimental data. Both resistivity and thermopower are well explained with these model potentials. It is probable that the remaining discrepancy comes from local screening and from the hard sphere structure factors. Indeed the experimental structure factor improves the resistivity for pure germanium and gallium. When calculating the thermoelectric power, we did not need to take into account the energy dependent contribution in the BHS model (a contribution that we have also neglected when using the SMP potential) because the pseudopotential is energy independent. The non-local contribution can be important, and the use of first-principles energy independent pseudopotentials represents progress in liquid alloy electronic property calculations. We consider our results to be very satisfactory and they confirm that the BHS form factor is adequate for describing the electronic properties of liquid metals and alloys.

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