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Temperature-dependent structure and electrical transport in liquid metals

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Abstract. A simple model has been considered to obtain the reversible temperature dependence of the static structure factors $S(q)$ for liquid metals. The measured values of $S(q)$ near the melting point have been utilised to obtain the same at elevated temperatures for Na, K, Mg, Zn, Al and Pb. The notion of Debye temperature in liquid metals has been discussed. The principal peak heights of $S(q)$ computed at the melting temperature have also been discussed in the light of Verlet's freezing rule. The electrical resistivity and thermo-electric power of these metals have been computed as a function of temperature. The success and failure of the Ziman formula have been critically assessed.

1. Introduction

The static structure factor $S(q)$ occurs as an important ingredient in the calculation of the electrical transport and thermodynamic properties of liquid metals. The structure and forces in liquid metals are also derivable (March 1987) from the knowledge of $S(q)$. The coordination number in the liquid metals is also determined from the area underneath the first peak (Waseda 1980). Verlet's freezing rule (Verlet 1968) further emphasises the importance of $S(q)$, and suggests that the first peak height of the structure factor reaches a value of about 2.8 at the freezing point.

Thus knowledge of the thermal dependence of $S(q)$ is of great importance to understand the behaviour of liquid metals near the melting point as well as at elevated temperatures. It is well known that $S(q)$ is experimentally determined by either x-ray or Neutron diffraction measurements, which involves an intricate process. Obviously the availability of $S(q)$ - T data is limited. We, therefore, attempt here a theoretical model to obtain the thermal dependence of $S(q)$.

It is well known that the positional correlation of atoms in the liquid state and in the amorphous state is relatively strong within the near-neighbour region. The same diffraction theory (Wagner 1978, 1980, Waseda 1980) has been used to deduce the structural disorder in liquids as well as in amorphous solids. The experiments have revealed that the diffraction pattern for the two states are quite similar. Recently Meisel and Cote (1977, 1978) have used a Van Hove (1954) dynamic structure factor to obtain a relation between $S(q)$ and T for amorphous materials. The same basic idea has been utilised here to obtain the thermal dependence of $S(q)$ for liquid metals. The results obtained for Na, K, Mg, Zn, Al and Pb are very encouraging.

The thermal dependence of $S(q)$ as obtained here has been utilised to compute the electrical resistivity and thermo-electric power of monovalent (Na, K) and polyvalent (Mg, Zn, Al, Pb) liquid metals as a function of temperature using Ziman's (1961) formula. The pseudopotential matrix elements required at different temperatures have been computed in the framework of fully non-local optimised model potential theory (Shaw 1968, Appapillai and Williams 1973).

We shall see in § 2 that $S(q)$ at other temperatures can be calculated from knowledge of the observed $S(q)$ at any given temperature. The results for Na, K, Al, Mg, Zn and Pb have been presented. In § 3, Verlet's freezing rule has been discussed in the context of the first peak height obtained at the freezing point. Further, the computed $S(q)$ - T values have been utilised in § 4 to compute the electrical resistivity and the thermo-electric power of liquid metals at elevated temperatures.

2. Temperature dependence of static structure factor

2.1. Basic relations

The static structure factor $S(q)$ may be defined by the integral of the coherent scattering law over all energy ($\hbar w$) transfers at constant q , i.e.

$$S(q) = \int_{-\infty}^{\infty} S(q, w) dw. \quad (1)$$

The coherent scattering law, $S(q, w)$, is usually known as the Van Hove (1954) dynamic structure factor and can be expanded in n -phonon terms like

$$S(q, w) = S_0(q, w) + S_1(q, w) + \dots \quad (2a)$$

$S_0(q, w)$ denotes the elastic term, i.e.

$$S_0(q, w) = a(q) \exp[-2W_T(q)] \delta(w) \quad (2b)$$

where $\exp[-2W_T(q)]$ is the Debye-Waller factor and

$$a(q) = N^{-1} \left\langle \sum_i \exp(-iq \cdot r_i) \sum_j \exp(iq \cdot r_j) \right\rangle. \quad (2c)$$

Here $\langle \rangle$ denotes the ensemble average over the ionic positions r_i and r_j . The phonon part $S_1(q, w)$ is defined as

$$S_1(q, w) = \exp[-2W_T(q)] \frac{n(-w)}{-w} \sum_{\alpha} \frac{\hbar q^2}{2M} [a(q - Q_{\alpha}) \delta(w - w_{Q_{\alpha}}) + a(q + Q_{\alpha}) \delta(w + w_{Q_{\alpha}})] \quad (3a)$$

where h is Planck's constant, M is the ionic mass and the sum runs over the α branch of the phonon spectrum. $n(w)$ is given as

$$n(w) = (e^x - 1)^{-1} \quad x = \hbar w / k_B T. \quad (3b)$$

In analogy with (2a), Meisel and Cote (1977) defined a model dynamic structure factor

Table 1. Debye temperature θ_D corresponding to solid and liquid metals.

Metal	Solid phase, θ_D^s (K)	Liquid phase, θ_D^l (K)	$(\theta_D^s - \theta_D^l)/\theta_D^s$ (%)
Na	158	111.5	29.4
K	163	50	69.3
Mg	290	175	39.6
Zn	250	172	31.2
Al	394	143	63.7
Pb	88	54.2	38.4

for amorphous and disordered solids and obtained a temperature-dependent static structure factor, i.e.

$$S_T(q) = a(q) \exp[-2W_T(q)] + A_T(q)\{1 - \exp[-2W_T(q)]\} \quad (4)$$

where $S_T(q)$ is the structure factor at temperature T . $A_T(q)$ is a coarse average of the structure factor $a(q)$ at all temperatures and can safely be approximated to $A_T(q) \rightarrow 1$. Thus from (4) one has

$$S_T(q) - 1 = [a(q) - 1] \exp[-2W_T(q)] \quad (5)$$

where $W_T(q)$ is the Debye–Waller factor

$$W_T(q) = \frac{3 \hbar^2 q^2 T}{2 M k_B \theta_D^3} \int_0^{\theta_D/T} [\frac{1}{2} + (e^z - 1)^{-1}] z dz. \quad (6)$$

Here θ_D is the characteristic temperature for liquid metals, which we will call the Debye temperature for convenience and will be treated as a parameter. Though the expression (4) has been specifically obtained for disordered solids, it can be safely used for other structurally disordered systems with suitable choice of θ_D . If $S_{T_1}(q)$ and $S_{T_2}(q)$ refer to structure factors at two different temperatures T_1 and T_2 then equation (5) can be expressed as

$$S_{T_1}(q) - 1 = [a(q) - 1] \exp[-2W_{T_1}(q)] \quad (7)$$

$$S_{T_2}(q) - 1 = [a(q) - 1] \exp[-2W_{T_2}(q)]. \quad (8)$$

Equations (7) and (8) enable us to write

$$S_{T_2}(q) = 1 + [S_{T_1}(q) - 1] \exp\{-2[W_{T_2}(q) - W_{T_1}(q)]\}. \quad (9)$$

Thus if the structure factor at any temperature T_1 is known, then the structure factor at the desired temperature T_2 can be calculated from equation (9).

2.2. Results

The observed (Waseda 1980) values of the structure factors at temperature T_1 have been used in equation (9) to compute the structure factors at other temperature T_2 . The only unknown quantity in the expression is the characteristic temperature θ_D , which has the same significance as the Debye temperature has in solid and amorphous phases. Obviously θ_D represents the character of the atomic motions in the liquid phase and has been assumed constant over the temperature range of interest. For want of better

knowledge of θ_D for liquid metals, we fixed it with the help of equations (6) and (9) to obtain the correct height of the principal peak in the structure factor at any given temperature. These are tabulated in table 1. We are tempted here to compare θ_D of the liquid metals obtained to that of the solid metals (Mott and Jones 1936). It is evident that θ_D of the liquid phase is less than that of the corresponding solid phase. This might be linked to the softening of phonons on melting. θ_D decreases by about 30% in Na and Zn and by about 40% in Mg and Pb. The maximum deviation occurs in Al and K, which is around 60%. In this context we draw attention to the fact (Faber 1972) that the frequency falls by some 40% in going from solid to liquid phase. Weiss (1984) has also qualitatively suggested the lowering of Debye temperature in liquids.

$S(q)$ computed for liquid metals Na (373, 473, 573 and 723 K), K (343, 378, 473 and 723 K), Mg (953, 1063, 1153 and 1173 K), Zn (723, 833, 933 and 1053 K), Al (943, 1023, 1173 and 1323 K) and Pb (613, 823, 1023 and 1173 K) at different temperatures are displayed in figure 1 and have been compared with the experimental values (Waseda 1980) wherever available. It may be emphasised that the same value of θ_D as in table 1 has been used in the calculation of $S(q)$ corresponding to different temperatures. The value obtained by the theoretical model and that by diffraction measurements are in very good agreement for Mg and Zn over a wide range of temperature. In the case of K overall agreement is quite good up to around 500 K but at higher temperature (723 K) our calculated $S(q)$ undergoes an abrupt fall in the first peak height unlike the observed value. The results for Na, Al and Pb are also in very good agreement with the observed values except at very high temperature where our first peak height is lower than the observed values.

The effect of temperature on $S(q)$ above the melting point is self-evident in figure 1. As we go up from the melting point, the peaks tend to become flatter and broader. The first peak height decreases gradually whereas its width increases on raising the temperature. The oscillation in $S(q)$ at higher q -values becomes progressively more damped and $S(q)$ tends to unity—a situation of completely random gas-like structure. Though the position of the first peak is not visibly affected, the area under the first peak (which characterises the coordination number) slightly decreases with rise in temperature. The values of the first peak height and its position as a function of temperature is tabulated in table 2.

3. Verlet's freezing rule

Verlet (1968) pointed out that the principal peak height of the static structure factor of liquids approaches a value of about 2.8 as the temperature is lowered to the freezing point. Usually Verlet's rule is tested against experimental data. But we may recall that the measured $S(q)$ normally corresponds to a temperature higher than the melting point. For example, the measured $S(q)$ for Mg refers to 953 K which is about 30 K higher than the melting point. The first peak height is very sensitive to temperature and therefore we estimate the same at the melting point from the model. In view of this, the present

Figure 1 (opposite). Static structure factor of liquid metals at different temperatures (full curves, present values; points, observed experimental values (Waseda 1980)): (a) Na at 373, 473, 573 and 723 K; (b) K at 343, 378, 473 and 723 K; (c) Mg at 953, 1063, 1153 and 1173 K; (d) Zn at 723, 833, 933 and 1059 K; (e) Al at 943, 1023, 1173 and 1323 K; and (f) Pb at 613, 823, 1023 and 1173 K.

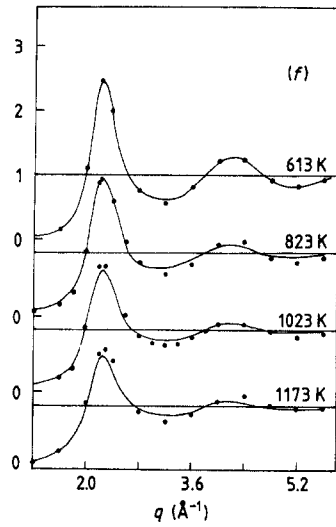
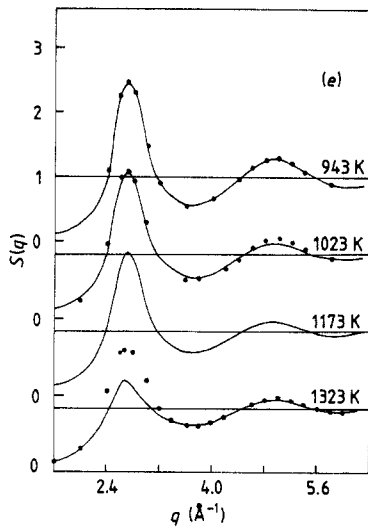
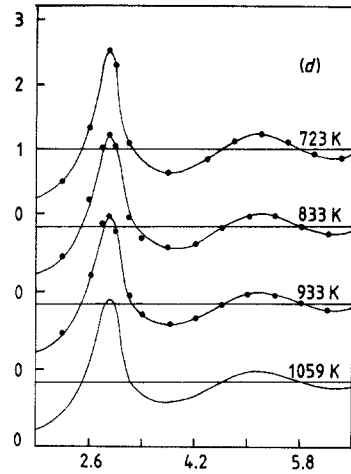
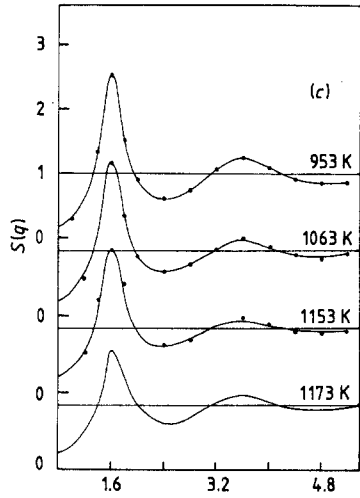
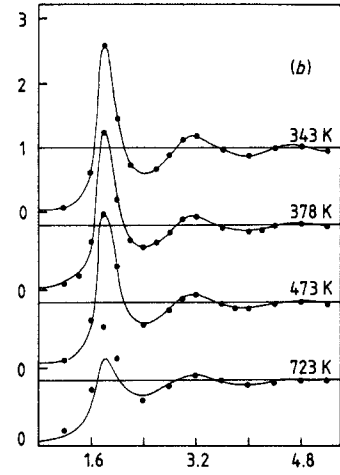
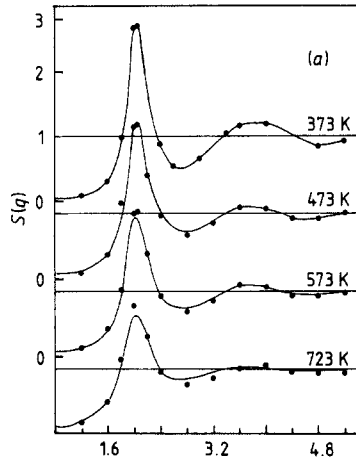


Table 2. The position and height of the first peak of $S(q)$ as a function of temperature.

Metal	T (K)	First peak height in $S(q)$	First peak position
Na	373	2.722	~2.027
	473	2.413	
	573	2.372	
	723	1.840	
K	343	2.622	~1.630
	378	2.448	
	473	2.406	
	723	1.374	
Mg	953	2.562	~2.420
	1063	2.402	
	1153	2.237	
	1173	1.881	
Zn	723	2.542	~2.900
	833	2.435	
	933	2.392	
	1050	2.285	
Al	943	2.476	~2.710
	1023	2.279	
	1173	2.240	
	1323	1.634	
Pb	613	2.492	~2.300
	823	2.158	
	1023	1.980	
	1173	1.760	

Table 3. Principal peak heights of the static structure factor at melting temperature (T_m).

Metal	Structure ^a	Melting temp., T_m (K)	Principal peak height	Second nearest peak height
Na	BCC	370.8	2.73	1.21
K	BCC	336.7	2.68	1.07
Mg	HCP	923.0	2.61	1.29
Zn	HCP	692.5	2.58	1.26
Al	FCC	932.0	2.51	1.31
Pb	FCC	600.4	2.51	1.32

^a This refers to solid-phase structure.

model, which provides a reversible temperature dependence of $S(q)$, has been used to compute the principal peak height of liquid metals down to the melting temperature and thus Verlet's rule has been tested. It has been observed that the principal peak height of $S(q)$ of liquid metals slowly increases with decrease in temperature.

The computed values of the principal peak height and second nearest peak height for Na, K, Mg, Zn, Al and Pb at the melting temperatures are recorded in table 3. The values indicate that the peak heights at the melting point depend slightly on the previous crystal structure. For BCC metals (Na, K) the principal height is around 2.7; for HCP

metals (Mg, Zn) it is around 2.6; whereas for FCC metals the first peak height approaches a value 2.5. Recently, March (1987) has also discussed Verlet's freezing rule in terms of the principal peak height of the static structure factor.

4. Electrical transport in liquid metals at elevated temperatures

Since the advent of the diffraction model (Krishnan and Bhatia 1945, Bhatia and Krishnan 1948, Ziman 1961) it has been widely used to compute the electronic properties of liquid metals near the melting point. But work at high temperature lags behind. In the past, some efforts have been made to study the thermal dependence of resistivity but most authors have considered that the pseudopotential matrix elements remain unchanged on thermal expansion (for reviews see Faber 1972, Shimoji 1977). But it is desirable that both structure factors and the pseudopotential matrix elements should be considered temperature-dependent in order to ascertain the applicability of Ziman's formula at elevated temperatures. By taking such effects into account, we have investigated the thermal dependence of the electrical resistivity and thermo-electric power of monovalent (Na, K), divalent (Zn), trivalent (Al) and tetravalent (Pb) liquids metals.

4.1. Electrical resistivity

Ziman (1961) showed that if the scattering of conduction electrons in liquid metals is treated in the Born approximation, then the resistivity R can be expressed as

$$R = (3\pi\Omega_0/e^2\hbar V_F^2)\langle S(q)|W(\mathbf{k}, \mathbf{q})|^2 \rangle \quad (10)$$

$$\langle \quad \rangle = \int_0^1 4S(q)|W(\mathbf{k}, \mathbf{q})|^2 \kappa^3 d\kappa \quad \kappa = q/(2k_F) \quad (11)$$

where e is the electronic charge, V_F is the Fermi velocity, $k_F = (3\pi^2 Z/\Omega_0)^{1/3}$ is the Fermi wavevector, $\Omega_0 = N/\Omega$ is the atomic volume and \mathbf{k} and \mathbf{q} are electron and phonon wavevectors. $S(q)$ is the static structure factor and $W(\mathbf{k}, \mathbf{q})$ are the screened pseudopotential matrix elements. In order to study the thermal dependence of R , one needs to know $S(q)$ and $W(\mathbf{k}, \mathbf{q})$ as functions of temperature. The $S(q)$ - T dependence has been discussed in detail in § 2 and it is this information which has prompted us to undertake the study of the present section. The values of $W(\mathbf{k}, \mathbf{q})$ as a function of temperature have been obtained using the energy-dependent non-local optimised model potential of Shaw (1968) because the latter has proved very successful in the study of electronic transport properties at the melting point.

The Shaw (1968) optimised model potential is in essence an improvement upon the well known Heine-Abarenkov (1964) form of the potential. In the former approach, the screened non-local pseudopotential matrix elements can be expressed as

$$W(k, q) = f(k, q) + \frac{4\pi}{\Omega_0 q^2 \epsilon^*(q)} [1 - G(q)]\rho + g(q) \left(1 - \frac{G(q)}{\epsilon^*(q)}\right) \quad (12)$$

with

$$f(k, q) = N \sum_{l=0}^{l_0} \langle k + q | (A_l(E) - z/r) p_l | k \rangle \quad (13)$$

$$g(q) = \frac{4}{\pi^2 q^2 \varepsilon(q)} \int_{k \leq k_F} \frac{f(k, q)}{k^2 - |k + q|^2} d^3 k \quad (14)$$

$$\varepsilon^*(q) = 1 + [\varepsilon(q) - 1][1 - G(q)] \quad (15)$$

where $\varepsilon(q)$ is the usual static Hartree dielectric function and $G(q)$ is the correction factor which arises due to exchange and correlation effects of the conduction electrons, for which the Vashishta and Singwi (1972) expression has been considered. Also ρ is the depletion hole and l_0 is the highest angular momentum to be modelled. For a given angular momentum, the energy-dependent model parameters $A_i(E)$ and $R_i(E)$ were determined by matching the logarithmic derivative of the wavefunction at the boundary, which in turn yield crystal parameters at $E = E_F$.

$W(k, q)$ have been computed through equation (12) in cylindrical coordinates following the work of Harrison (1966) at $|\mathbf{k} + \mathbf{q}| = |\mathbf{k}| = k_F$. The atomic volume Ω_0 and k_F have been chosen appropriate to the temperature of investigation. The temperature-dependent values of $W(k, q)$ and $S(q)$ are now subjected to equation (10) to infer electrical resistivity as a function of temperature.

The values of electrical resistivity computed as a function of temperature for Na, K, Zn, Al and Pb are displayed in figure 2 and are compared with the experimental observations (for Na and K (Freund 1969); for Zn, Al and Pb (Roll and Motz 1957)). The resistivity of these liquid metals increases almost linearly with increasing temperature. Theory and experiment agree well near the melting point but the discrepancies widen at high temperatures. The results for K and Zn provide a better picture than for Na, Al and Pb. It is obvious that Ziman's formula predicts the linear dependence of R but is unsuccessful in yielding the magnitude of the gradient ($\partial R/\partial T$). The computed values of the resistivity coefficient

$$\alpha = [R(T) - R(T_m)]/(T - T_m)R(T_m) \quad (16)$$

are tabulated in table 4 along with experimental values. Except for K and Zn, the resistivity coefficients computed for other metals are much smaller than the experimental values. There are many possible causes for the discrepancies. First the experimental data on electrical resistivity itself are not unique (Cusack 1987). But nonetheless if we assume the validity of the experimental data then the following discussion follows.

In order to obtain closer agreement at high temperatures, one requires larger values of $\langle S(q)|W(k, q)|^2 \rangle$, which means that $S(q)$ and $W(k, q)$ should be greater than the present values. Even the use of measured $S(q)$ in the calculation of resistivity is not expected to improve the result as the observed and computed $S(q)$ are in very good agreement in the temperature range of our investigation. As the probability of error in $S(q)$ is very small, the improvement is only possible through $W(k, q)$. But such a large discrepancy is not expected to be lessened through any sort of improvement in $W(k, q)$. Then what we are left with is the weaknesses inherent in Ziman's (1961) formula. It is likely that at temperatures above the melting point, the kinetic energy of the particles increases, which gives rise to strong scattering in the system. If that is the case, then the latter might be responsible for the observed discrepancies because Ziman's formula does not take into account strong scattering.

The result for sodium is more surprising to us. There is almost exact agreement near the melting point but the discrepancy increases with increasing temperature. Being monovalent, Na is known for its simplicity and has been a favourite candidate for the application of pseudopotential theory near the melting point. In spite of the fact that

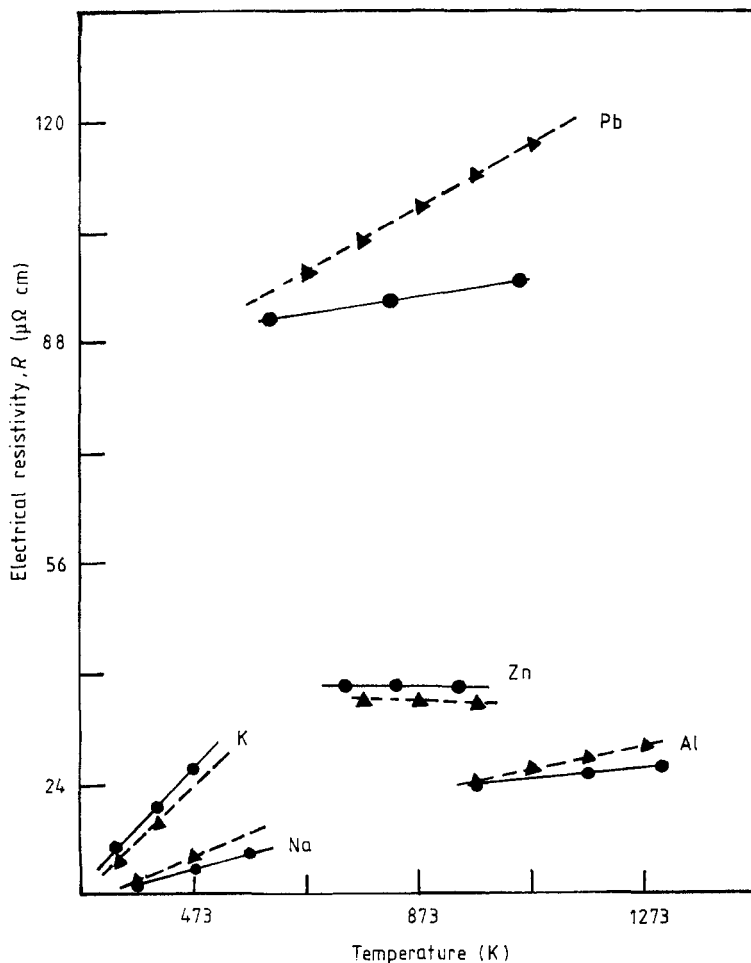


Figure 2. Temperature dependence of electrical resistivity of Na, K, Zn, Al and Pb: full circles and full curves, theory; triangles and broken curves, experimental values (Na and K (Freund 1969); Zn, Al and Pb (Roll and Motz 1957)).

Table 4. Resistivity coefficient of liquid metals.

Metal	Electrical resistivity coefficient (K^{-1})	
	$\alpha_{\text{theor}} \times 10^{-3}$	$\alpha_{\text{expl}} \times 10^{-3}$
Na	2.9	5.7
K	5.7	4.27
Zn	-0.026	-0.084
Al	0.144	0.475
Pb	0.131	0.534

both $W(k, q)$ and $S(q)$ have been considered temperature-dependent, we have failed to obtain a desired gradient for Na. In view of this, we emphasise that the other properties of sodium at higher temperature should be carefully analysed.

Table 5. Thermo-electric power coefficient of liquid metals.

Metal	Temp. (K)	Thermo-power coefficients	
		x_{theor}	x_{expt}
Na	373	2.80	2.72 ^a
	573	2.87	2.74 ^a
K	338	2.50	3.42 ^a
	408	2.53	3.32 ^a
Zn	743	-2.55	-0.20 ^b
	903	-2.47	-0.44 ^b
Al	976	1.056	0.955 ^b
	1302	1.23	0.957 ^b
Pb	613	2.73	2.11 ^b
	1053	2.77	2.115 ^b

^a Kendall (1968).^b Marwaha and Cusack (1966).

4.2. Thermo-electric power

At a given temperature T , the thermo-electric power Q can be written as (Bradley *et al* 1962)

$$Q = -(\pi^2 k_B^2 T/3|e|)(\partial \ln R(E)/\partial E)_{E=E_F} \quad (17)$$

where the terms have their usual meaning. The bracketed term on the right-hand side is called the thermo-power coefficient (X). Applying equation (10) to equation (17) one readily obtains

$$X = 3 - 2P - r/2 \quad (18)$$

$$P = |W(k_F, 2k_F)|^2 S(2k_F) / \langle S(q) |W(k_F, q)|^2 \rangle \quad (19)$$

$$r = k_F \langle a(q)(\partial/\partial k) |W(k, q)|^2 \rangle_{k_F} / \langle S(q) |W(k_F, q)|^2 \rangle \quad (20)$$

where $\langle \rangle$ stands for the same as in equation (11). Here r results from the energy dependence of the pseudopotential and is usually very small. In order to understand X - T behaviour qualitatively, here we have dropped the r term.

The computed values of X for Na, K, Zn, Al and Pb are tabulated in table 5 along with experimental observations. The theoretical values of Na, K, Al and Pb are in reasonable agreement with the experimental values. The values of X for Zn are much lower than the observed values but the correct sign has been reproduced. It is obvious that, unlike electrical resistivity, X depends only moderately on temperature and thus could be explained by the theory. The R - T discrepancy is being overcome here due to the term $(\partial \ln R(E)/\partial E)_{E=E_F}$.

5. Conclusions

The present study on the reversible thermal dependence of the static structure factor $S(q)$ and the transport properties of liquid metals suggest the following:

(i) It is possible to obtain the $S(q)$ values of liquid metals at different temperatures with fair success by using the experimentally observed values of the same at any given temperature.

(ii) The principal peak heights in $S(q)$ obtained at the melting point seem to depend moderately on the corresponding solid-phase crystal structure. The computed values of the principal peak heights are slightly lower than those obtained from Verlet's freezing rule.

(iii) Ziman's formula of electrical resistivity yields small values for the resistivity coefficient for Na, Al and Pb even though the pseudopotential matrix elements and the structure factors are duly considered temperature-dependent.

(iv) The thermo-electric power depends moderately on temperature and could be explained successfully on the basis of Ziman's formula.

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