Theoretical study of the temperature dependences of electronic magnetic susceptibilities for liquid lithium and sodium

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Abstract. In the context of the nearly-free-electron model, we apply a full non-local model pseudopotential theory to investigate the temperature dependence of the electronic magnetic susceptibility for liquid lithium and sodium. In contrast to previous and recent theoretical calculations, we adopt the accurate generalized non-local model pseudopotential of Li *et al* to simulate self-consistently the liquid structure factors of both metals. Within the nearly-free-electron theory, we find that the ion-potential alone is not sufficient to explain the temperature trend of the electronic magnetic susceptibility. Nonetheless, by seriously considering the many-body electron–electron exchange correlation and analysing its temperature change, we are able to understand certain features of the susceptibility as observed in recent experiments. The limitation of our theoretical model will also be indicated.

1. Introduction

Recently the temperature dependence of the electronic magnetic susceptibility of simple liquid metals has attracted the attention of experimentalists (Shimokawa *et al* 1986, 1988, Marel *et al* 1988, Warren *et al* 1984, El-Hanany *et al* 1983, Nicoloso and Freyland 1983, Bottyan *et al* 1983, Hanabusa *et al* 1976, Freyland 1979, Collings 1965) and theorists (Lai 1989, Chapman and March 1988, Kelly and Glotzel 1986, Franz 1984, Wang *et al* 1980, Takahashi and Shimizu 1973a, b). The interest of the researchers falls into two categories. In one category, emphasis is placed on the studies of magnetic susceptibility of expanded liquid metals and the eventual goal of the research is to obtain further insight into the electronic correlation mechanism at sufficiently high temperature (or low electron density). This study leads to an understanding of the metal–non-metal transition. For investigation in this area there seems to have been no quantitative theory giving a microscopic picture of the observation. In the second category, much effort has been devoted to the consideration of the temperature changes of the electronic magnetic susceptibility (to be referred to as χ hereafter) in the temperature regime close to the melting point. Differing from the study of expanded liquid metals, this latter field of research can be investigated using a theoretical model somewhat quantitatively. The purpose of this work parallels the direction of the second category.

Starting from a nearly-free-electron model (Lai *et al* 1978, Wang *et al* 1980, Iwamatsu *et al* 1983) we first carry out a detailed analysis of the effects of ion potential on the temperature behaviour of χ for liquid lithium and sodium metals. It will be shown that the influences of the random arrays of ions on χ is generally small. Accordingly, considering this contribution alone is ineffective in explaining both the magnitude and the trend for the temperature dependence of χ. To be able to make further progress, we propose a method which combines the jellium spin susceptibility, the Landau theory of Fermi liquid and the density-of-states effective mass. As it stands, this method takes into account explicitly the temperature dependences of the exchange-correlation correction of conduction electrons to the spin paramagnetic susceptibility. Within the approximation used in this work, we are capable of describing the temperature variation of χ for the liquid Li satisfactorily. Furthermore, when the same approach is applied to liquid metal Na, our calculation predicts a temperature trend in χ in agreement with the measurements of Shimokawa *et al* (1986), Bottyan *et al* (1983), Takeda and Tamaki (1989). However, at $T > 350\,^\circ\mathrm{C}$, the anomalous enhancement of χ for Na is inexplicable using the present theoretical model.

The presentation of this paper is as follows. In section 2, we review briefly the nearly-free-electron model approach to χ and carry out a derivation in the context of the generalized non-local model pseudopotential (GNMP) theory of Li *et al* (1986, 1987). We describe how essential it is to take proper account of the temperature dependences of the exchange-correlation correction of valence electrons in χ. Numerical computation follows in section 3 where we present the results of our calculations separately for liquid metals Li and Na. Finally, in section 4 we give a summary of our present work.

2. Electronic magnetic susceptibility theory

In this section we first outline the calculation of χ using a perturbation method. As mentioned above, the derivation will be carried out in the spirit of GNMP theory (Li *et al* 1986, 1987).

To begin with, we consider the equation for a valence electron in a liquid metal. In the presence of a weak magnetic field ($B = B\hat{z}$) one may write the Hamiltonian for such a system as

$$H = (1/2m)[p - (e/c)A]^2 + \mu_B B \sigma_z + W(r) = h_0 + W(r) \tag{1}$$

where A is the vector potential, p and m are, respectively, the electronic momentum and mass, μ_B is the Bohr magneton and σ_z is the z component of the Pauli spin operator. In equation (1) $W(r)$ is an electronic pseudopotential describing the interaction of an electron with all the ions. Here we refer the interested readers to the work of Lai *et al* (1978) for a justification of the introduction of a pseudopotential into equation (1). To proceed with our perturbative calculation, we note that the unperturbed wavefunction of h_0, i.e., $|nk_xk_zm_s\rangle$ with $|m_s\rangle$ a spin state and $|n\rangle$ given by

$$|n\rangle = (a/2^n n! \sqrt{\pi})^{1/2} \exp[-a^2(y - y_0)^2/2] H_n[(y - y_0)a] \tag{2}$$

where $a^2 = 2eB\pi/hc$, $y_0 = -hck_x/2\pi eB$, H_n is the nth Hermite polynomial, $|k_j\rangle =$

$V^{-1/6} \exp(-ik_j j)$, $j = x, z$ and V is the volume of the metal under consideration, which has been used to rewrite W as

$$W = \sum_{n,k_x,k_z} |nk_x k_z\rangle\langle nk_x k_z| W |nk_x k_z\rangle\langle nk_x k_z|$$

$$+ \sum_{n,k_x,k_z} \sum_{n',k_x',k_z'}{}' |nk_x k_z\rangle\langle nk_x k_z| W |n' k_x' k_z'\rangle\langle n' k_x' k_z'|$$

$$= \sum_{n,k_x,k_z} |nk_x k_z\rangle\langle nk_x k_z| W |nk_x k_z\rangle\langle nk_x k_z| + W'. \tag{3}$$

As can be shown easily, the first term in equation (3) plus h_0 commutes with the original h_0. The unperturbed wavefunction is therefore the same as it would have been for h_0, the only modification being that the unperturbed energy now takes on $(E_0 + \langle nk_x k_z| W |nk_x k_z\rangle)$ in which E_0 satisfies $h_0 |nk_x k_z\rangle = E_0 |nk_x k_z\rangle$.

To continue, we calculate the partition function of the present problem. By taking the unperturbed Hamiltonian as

$$H_0 = h_0 + \sum_{n,k_x,k_z} |nk_x k_z\rangle\langle nk_x k_z| W |nk_x k_z\rangle\langle nk_x k_z| \tag{4}$$

the partition function can be written as

$$Z(\gamma) = \mathrm{Tr}\{\exp[-\gamma(H_0 + W')]\} \qquad \gamma = 1/k_B T. \tag{5}$$

Treating W' as a weak perturbation, the Schwinger formula (Glasser 1964) can be used to expand $Z(\gamma)$ in the form

$$Z(\gamma) = \mathrm{Tr}[\exp(-\gamma H_0)] - \gamma \mathrm{Tr}[W' \exp(-\gamma H_0)]$$

$$+ (\gamma^2/2) \mathrm{Tr}\left[\int_0^1 du\, W' \exp[-\gamma H_0(1-u)]W' \exp(-\gamma H_0 u)\right] + \dots. \tag{6}$$

Though tedious, each of the terms on the right-hand side of equation (6) can be calculated straightforwardly (see Lai *et al* (1978) for details). Once $Z(\gamma)$ has been determined, we may go on to derive the thermodynamic potential, Φ, per unit volume. The technique used in this part of the calculation is to observe that Φ and $Z(\gamma)$ are related via the inverse Laplace transform

$$\Phi = \int_0^\infty ds\, \bar{Z}(s) \frac{\partial f}{\partial s} \tag{7}$$

with

$$\bar{Z}(s) = \frac{1}{2\pi i} \int_{C-i\infty}^{C+i\infty} dt\, \frac{Z(t)}{t^2} e^{st} \qquad C > 0 \tag{8}$$

and f the Fermi distribution function. At temperatures which are low compared with the Fermi temperature, $\partial f/\partial s$ in equation (7) can be replaced by a delta function. Φ can then be simplified and expressed in a power series function of the magnetic field B. In particular, in a weak magnetic field we may keep B up to second order. The electronic magnetic susceptibility can thus be calculated using $\chi = -(\partial\Phi/\partial B)/B$.

The above procedure has been applied in conjunction with the GNMP theory of Li *et al* (1986, 1987). The calculated electronic magnetic susceptibility of a simple liquid metal can be cast in the form (Lai *et al* 1978, Lai 1989)

$$\chi = \chi_0(1 + \Delta). \tag{9}$$

Here χ_0 is the familiar Landau–Pauli free electron susceptibility and $\Delta = \delta^{(0)} + \delta_C$ is a term describing the perturbation of the ion potential on the χ of valence electrons. In the context of GNMP theory both $\delta^{(0)}$ and δ_C can be derived as (Lai *et al* 1978)

$$\delta^{(0)} = -\frac{3Z}{32\eta_0^2} \int_0^\infty dp\, S(pk_F) w_{-pk_F}(k_F + pk_F) w_{pk_F}(k_F)$$

$$\times \left[2(p - p^{-1}) \ln \left| \frac{p + 2}{p - 2} \right| - \frac{8}{3} \frac{(3p^4 - 7p^2 - 12)}{(4 - p^2)^2} \right] \tag{10}$$

$$\delta_C = \frac{\partial w_0(k_F)}{\partial \eta} \left(\frac{1}{3} + \frac{3Z}{16\eta_0^2} \int_0^\infty dp\, pS(pk_F) w_{-pk_F}(k_F + pk_F) \right.$$

$$\left. \times w_{pk_F}(k_F) \ln \left| \frac{p + 2}{p - 2} \right| \right) - \frac{3Z}{16\eta_0} \int_0^\infty dp\, [p^2 + 4^{-1}p(4 - p^2)]$$

$$\times \ln \left| \frac{p + 2}{p - 2} \right| S(pk_F) \frac{\partial}{\partial \eta} [w_{-pk_F}(k_F + pk_F) w_{pk_F}(k_F)] \tag{11}$$

in which $\eta_0 = k_F^2/2$, k_F is the Fermi wavevector, Z is the nominal valence, η is the chemical potential perturbed by the ion potential, $S(q)$ is the liquid structure factor characterizing the equilibrium ionic distribution and, finally, $w_q(k_F) = \langle k_F + q | w | k_F \rangle$ and $w_{-q}(k_F + q) = \langle k_F | w | k_F + q \rangle$ are the on-Fermi-level form factors constructed using the GNMP theory. At a given temperature and density, Δ can be evaluated readily.

Now, equation (9) only accounts for the ion potential effects on the χ of valence electrons. This contribution, as is demonstrated below, is generally not significant enough to explain the observed susceptibility. To compare the calculated susceptibility with experiment, it is necessary to take into account the effect of temperature dependences of the exchange correlation of conduction electrons. Following our previous and recent works (Lai *et al* 1978, Lai 1989) we estimate such a many-body electron–electron interaction by taking the difference between the spin susceptibility χ_p^* in the Landau theory of a Fermi liquid and the $(m^*/m)\chi_{pf}$, χ_{pf} being the free electron Pauli susceptibility, in the effective mass approximation. In terms of χ_0, this contribution can be written

$$\delta_{EC}\chi_0 = -(3m^*/2m)[1/(1 + 1/B_0)]\chi_0. \tag{12}$$

In the above equation B_0† is the Landau spin-interaction coefficient (Pines and Nozieres 1966, Plazman and Wolff 1973) including the effect of electron–electron interactions and the influence resulting from the liquid disorder of ions. Accordingly, m^* is the effective mass (which may be taken to be the density-of-states effective mass at the Fermi surface (Lai and Wang 1982, Lai *et al* 1981)) of an electron in a liquid metal. It should be stressed at this point that while taking our exchange-correlation correction to

† We emphasize that in the case of a solid metal m^* is the electronic density of states effective mass including both the effects of the electron–electron and electron–phonon interactions. In a liquid metal the appropriateness of using this Landau paramagnetic susceptibility formula can be inferred from the previous work by Wang and So *et al* (1977) (see also Lai *et al* (1978), Iwamatsu *et al* (1983) for further evidence).

be δ_{EC}, we have in fact assumed negligible contribution for the diamagnetic part (see Lai (1989) for reasons).

Before proceeding to the numerical calculation of χ we would like to point out that in this paper the Landau parameter B_0 has been calculated using a novel method (Lai 1989). The basic idea of the method is to first note that the spin paramagnetic susceptibility for a real metal can be written as (Silverstein 1963, Stoll *et al* 1971, Takahashi and Shimizu 1973a, b, Pines 1955)

$$\chi_p^* = \chi_{EC}/[1 + (m/m^* - 1)\chi_{EC}/\chi_{pf}] \tag{13}$$

where m^*, consistent with that defined below equation (12), is the electronic density of states effective mass for an electron in a liquid metal (see, for example, Takahashi and Shimizu 1973b). χ_{EC} and χ_p^* are, respectively, the jellium (which includes the electron–electron exchange-correlation effects alone) and the real metal (which considers both the exchange correlation and the influence of ion potential) spin susceptibilities. On the other hand, as given by equation (12), χ_p^* can also be shown within the Landau–Fermi liquid theory as

$$\chi_p^* = (m^*/m)\chi_{pf}/(1 + B_0). \tag{14}$$

By virtue of equations (13) and (14), one readily obtains

$$B_0 = (m^*/m)[(\chi_{pf}/\chi_{EC}) - 1]. \tag{15}$$

Obviously B_0 depends on m^*/m as well as on χ_{EC}/χ_{pf}. The former quantity can be evaluated as in Lai and Wang (1982). For the latter quantity, we have adopted the theoretical results of Kojima and Ishihara (1979) and Wilk and Vosko (1981) following a critical review by Kushida *et al* (1976).

3. Numerical results and discussion

We have applied equations (9)–(12) and (15) to the calculation of χ for liquid metals lithium and sodium. For both liquid metals the GNMP theory, which includes higher (than second) order corrections, has been adopted to account for the electron–ion interaction. For the case of Li, the higher-order correction is certainly indispensable because the valence electrons of lithium are essentially 2p-like and there are no p-core states to prevent these p-valence electrons coming near the nucleus. For this metal we have, in addition, incorporated the possible state-mixing effects for the s and p valence electrons (see Li *et al* (1987) for details). To proceed to the computation, it remains to mention three further pieces of information. The first is that in extracting the experimental electronic molar susceptibilities we have to subtract the ionic susceptibility from the measured χ data. In this work the values due to Angus (1932) were employed in the estimation. Secondly, we need the metallic densities at different temperatures for liquid metals Li and Na. We have taken these quantities from Crawley (1974), Huijben *et al* (1975), Ruppersberg and Speicher (1976), Berezhkovsky *et al* (1984), Borgstedt and Mathews (1987). Thirdly, we require, at each temperature, the liquid structure factor for both liquid metals. Here, as in preceding work (Lai 1989), we input the same GNMP interatomic pair potential and determine these $S(q)$s self-consistently using the Monte Carlo simulation (Lai 1988). In the following we discuss the $\chi(T)$ of the two liquid metals separately.

Table 1. Temperature T, density parameter r_s, density-of-states effective mass m^*/m, Landau coefficient B_0 and spin susceptibility χ_p^* for liquid Li. KI and WV refer to susceptibilities calculated using Kojima and Ishihara (1979) and Wilk and Vosko (1981), respectively. Experimental values near the melting point are estimated from Samble *et al* (1985) and Enderby *et al* (1964).

$T(K)$	r_s	m^*/m	$-B_0^{KI}$	$-B_0^{WV}$	$\chi_{p,KI}^*$	$\chi_{p,WV}^*$	$\chi_{p,expt}$
470	3.3096	1.416	0.4240	0.4778	1.924	2.122	2.43 ± 0.21
595	3.3398	1.383	0.4171	0.4699	1.840	2.023	—
725	3.3724	1.353	0.4111	0.4628	1.765	1.935	—
800	3.3919	1.337	0.4078	0.4590	1.724	1.887	—
900	3.4185	1.314	0.4031	0.4535	1.668	1.821	—

3.1. Lithium

The results of our calculations for this metal are depicted in figure 1. A glance at the figure shows that our present calculation using GNMP theory predicts a decrease in molar susceptibility χ versus temperature. This temperature dependence of χ is compatible with the observed data of Shimokawa *et al* (1986) and Marel *et al* (1988) not only in temperature variation but also in absolute magnitudes. In order to appreciate the results quantitatively, we present in table 1 (a) our calculated B_0 and the corresponding spin paramagnetic susceptibility, χ_p^* and in table 2 (b) various contributions to χ.

Let us first examine table 1. There are two points to be noted. First, we see that at temperatures above and near the melting point the calculated Landau spin-interaction parameters B_0 are all larger than those determined experimentally in the solid phase (at low temperature $B_0 \simeq -0.2$, see, for example, Dunifer *et al* (1974, 1978, 1984, 1985), Knecht (1975), Flesner and Schultz (1976), Vier *et al* (1984), Witt and VanderVen (1979)). Second, we find that χ_p^* calculated in the context of Fermi liquid theory, viz,

$$\chi_p^* = (m^*/m)\chi_{pf}/(1 + B_0) \tag{16}$$

(with B_0 obtained from equation (15)) compares favourably with available experiments. To explain these two points, we note first of all that the effective mass of an electron decreases manifestly from $2.21 \sim 2.34$ (Dunifer *et al* 1985) at low temperature to approximately 1.4 (see also table 1) in the liquid state. On the other hand, since the spin susceptibility of lithium varies negligibly upon melting (Enderby *et al* 1964, Hanabusa *et al* 1976), it is intuitively plausible that $|B_0|$ in equation (15) has to increase to compensate for such behaviour in χ_p^*. Now the question is, does the B_0 given in table 1 yield the correct order of magnitude? Is there any experimental evidence or indication that supports or refutes the present theoretical estimates? In order to delve into these puzzles, it is of interest to draw upon an experimental work of Flesner and Schultz (1976). In their transmission-electron-spin-resonance experiment on Li in combination with the resistivity data, these authors succeeded in extracting the value of the Landau coefficient B_0^{ee}, a parameter that includes only the electron–electron interaction. According to their analysis, the extracted B_0^{ee} is a very informative parameter for it can be utilized to determine B_0 at any temperature (much lower than the Fermi temperature) provided the effective mass of an electron is known. Since the valence electron gas at the temperature regime covered in this work is still highly degenerate, we may substitute the m^*/m given in table 1 into (Flesner and Schultz 1976, Lai 1989)
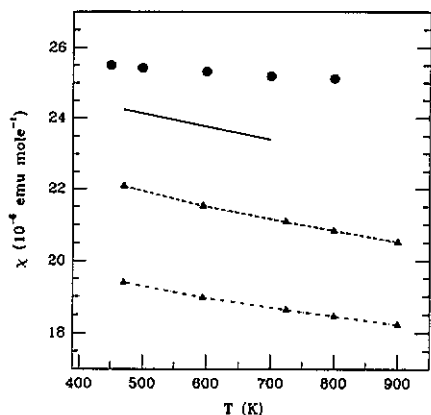
$$B_0 = (m^*/m)(1 + B_0^{ee}) - 1 \tag{17}$$

Figure 1. The electronic molar magnetic susceptibility versus temperature for liquid lithium. Broken curve: WV results; chain curve: KI results; solid circles: experiment (Marel *et al* 1988); full line: experiment (Shimokawa *et al* 1986).
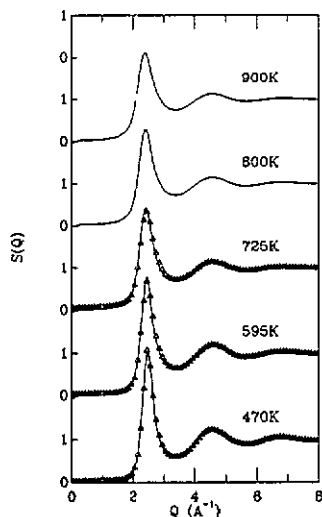
Figure 2. Liquid structure factors for lithium computed using Monte Carlo simulation (denoted by full curves) compared with experimental data (denoted by empty triangles) taken from Olbrich *et al* (1983).

Table 2. Corrections from ion-potential $\delta^{(0)}$, δ_C and $\Delta = \delta^{(0)} + \delta_C$, many-body electron-electron interactions δ_{EC} to the total electronic magnetic susceptibilities χ for liquid Li. KI and WV refer to δ_{EC} calculated respectively from Kojima and Ishihara (1979) and Wilk and Vosko (1981).

T (K)	$\delta^{(0)}$	$-\delta_C$	Δ	δ_{EC}^{KI}	δ_{EC}^{WV}
470	0.3125	0.1344	0.1781	1.563	1.944
595	0.2756	0.1283	0.1473	1.484	1.839
725	0.2427	0.1227	0.1200	1.417	1.748
800	0.2256	0.1198	0.1058	1.381	1.702
900	0.2023	0.1160	0.0863	1.331	1.636

and estimate, semi-empirically, the Landau coefficient B_0. Near the melting temperature we find that $B_0 = -0.55 \pm 0.04$. This value is of order of magnitude comparable with the one displayed in table 1.

Coming to table 2, we have two comments on the calculated entities. In the first place, it is noticeable that the influence of the ion potential on the χ of valence electrons is an order of magnitude greater than those in liquid metals Cs (Lai 1989) and Na (see below). As these Δs themselves are quite reliable and accurate (consult Li *et al* (1987) for the justification of pseudopotential and figure 2 for simulated $S(q)$) compared with corresponding ones obtained previously in low-order perturbation theory along with the hard sphere Percus–Yevick $S(q)$, we interpret any disparity in χ between theory and observed data to be associated with our underestimation of B_0 (probably through χ_{EC}/χ_{pf}). The second comment that we wish to make is that the Δ obtained here differs in

Table 3. Temperature T, density parameter r_s, density-of-states effective mass m^*/m, Landau coefficient B_0 and spin susceptibility χ_p^* for liquid Na. KI and WV refer to susceptibilities calculated using Kojima and Ishihara (1979) and Wilk and Vosko (1981), respectively. Experimental values near the melting point are taken from Dupree and Seymour (1972).

T (K)	r_s	m^*/m	$-B_0^{KI}$	$-B_0^{WV}$	$\chi_{p,KI}^*$	$\chi_{p,WV}^*$	$\chi_{p,expt}$
373	4.0479	1.086	0.3787	0.4197	1.118	1.197	1.1
423	4.0654	1.083	0.3788	0.4197	1.111	1.189	—
473	4.0834	1.080	0.3791	0.4198	1.103	1.181	—
573	4.1177	1.074	0.3793	0.4197	1.088	1.164	—
723	4.1737	1.065	0.3801	0.4199	1.066	1.139	—
823	4.2130	1.059	0.3806	0.4200	1.051	1.122	—

Table 4. Corrections from ion-potential $\delta^{(0)}$, δ_C and $\Delta = \delta^{(0)} + \delta_C$, many-body electron–electron interactions δ_{EC} to the total electronic magnetic susceptibilities χ for liquid Na. KI and WV refer to δ_{EC} calculated, respectively, from Kojima and Ishihara (1979) and Wilk and Vosko (1981). Experimental electronic volume magnetic susceptibilities χ_{expt} are read from figure 1 in Bottyan *et al* (1983). Units for χ are 10^{-6} cgs volume.

T (K)	$\delta^{(0)}$	$-\delta_C$	Δ	δ_{EC}^{KI}	δ_{EC}^{WV}	χ^{KI}	χ^{WV}	χ_{expt}
373	0.0464	0.0166	0.0297	0.993	1.178	0.863	0.942	0.777
423	0.0436	0.0163	0.0274	0.991	1.175	0.857	0.935	0.773
473	0.0403	0.0159	0.0243	0.989	1.172	0.851	0.929	0.771
573	0.0350	0.0153	0.0197	0.985	1.165	0.840	0.916	0.767
723	0.0271	0.0144	0.0128	0.980	1.156	0.824	0.897	0.771
823	0.0226	0.0138	0.0088	0.976	1.150	0.814	0.885	0.776

sign from those of liquid Cs. We attribute this reversal in sign to a possible cancellation between the pseudopotential and $S(q)$ (Timbie and White 1970). We further emphasize that in order to explain the experimental $\chi(T)$, δ_{EC} needs to decrease with temperature, as indeed is borne out in our calculation.

3.2. Sodium

In contrast to the case of liquid metal Li, the measured electronic molar magnetic susceptibility of liquid Na (Shimokawa *et al* 1986, Bottyan *et al* 1983, Takeda and Tamaki 1989), given in figure 3, shows a trend towards a slight increase in temperature. Our calculated χ using either the Kojima–Ishihara (Kojima and Ishihara 1979) or the Wilk–Vosko (Wilk and Vosko 1981) version of χ_{EC}/χ_{pf} agrees with these measured values. As in liquid Li, we can analyse our χ quantitatively by displaying various input parameters (table 3) and contributions (table 4) to χ. It is interesting to note first from table 4 that the effects resulting from the disordered array of ions (the Δ term) on the conduction electrons are also opposite in sign with respect to corresponding ones obtained for the liquid metal Cs. In particular, the calculated $|\Delta|$s are found to be a factor of two smaller than those of Cs. These differences in Δ between liquid metals Na and Cs can be easily understood and are attributed to the stronger dependence on non-locality of the pseudopotential for the liquid Cs than for the Na. At this point we should mention that
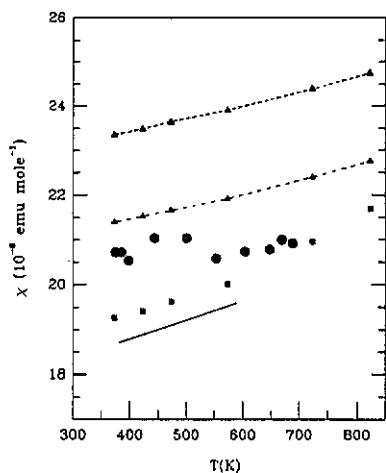
Figure 3. The electronic molar magnetic susceptibility versus temperature for liquid sodium. Broken curve: WV results; chain curve: KI results; full circles: experiment (Takeda and Tamaki 1989); full squares: experiment (Bottyan *et al* 1983); full line: experiment (Shimokawa *et al* 1986).
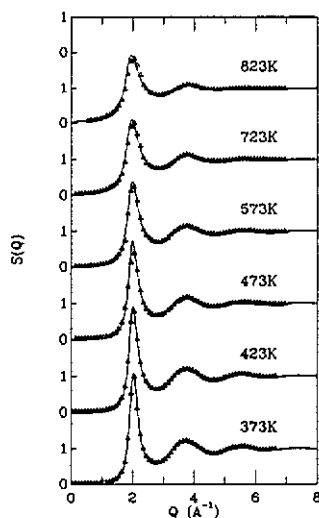
Figure 4. Liquid structure factors for sodium computed using Monte Carlo simulation (denoted by full curves) compared with experimental data (denoted by empty triangles) taken from Huijbin and van der Lugt (1979) and Waseda (1980).

the $|B_0|$ given in table 3 is virtually constant and is weakly increasing in contrast to those of liquid metals Li and Cs (see table 1 and Lai (1989)). Specifically, we emphasize that the estimated magnitudes of B_0 are also in order (at the melting point compare the observed $B_0 \simeq -0.32 \pm 0.08$ (demonstrated in Lai (1989)) with that given in table 3 and also the theoretical and experimental χ_p^* given in the same table). We finally remark that although the GNMP theory is capable of predicting the $S(q)$ of Na reasonably well at various temperatures (see figure 4), our calculation breaks down when used to attempt to explain the observed anomalous enhancement of χ at $T > 350$ C (Bottyan *et al* 1983). To see this, in table 4 we compare our calculated electronic volume susceptibility χ with that of Bottyan *et al* (1983); our theoretical χ shows a monotonic decrease in temperature up to $T = 550$ C whereas the experimental χ starts to increase rapidly at T about 350 C and beyond. This implies that the mechanism characterizing the drastic increase in χ with temperature can not be due to the ion potential and the many-body electron–electron interaction as discussed here; other physical mechanisms such as the intra-atomic strong electron correlation (Brinkman and Rice 1970) intimately interlaced with the incipient of antiferromagnetic behaviour could be the physics behind the phenomenon.

4. Conclusion

A full non-local pseudopotential perturbation theory was applied to study the temperature dependence of the electronic magnetic susceptibility for liquid metals Li and Na. Despite our efforts to improve upon our input sources, such as by the use of an

accurate non-local pseudopotential, by the self-consistent determination of the liquid structure factors via computer simulations etc, we find that the effect of ion potential on the χ of valence electrons is generally too small in magnitude. This prompts us to consider the temperature dependence of the many-body electron–electron exchange-correlation correction to χ. For both liquid metals Li and Na, our calculated molar susceptibility $\chi(T)$ is in reasonably good agreement with experiment, both in magnitude and in temperature trends. Our theoretical model for liquid metal Na fails to explain the anomalous enhancement of χ at much higher T. Further study of the electron correlation mechanism may help to resolve such an anomaly.

Acknowledgments

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