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Nearly-Free-Electron Susceptibility of Liquid Metals*

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The magnetic susceptibility of a liquid metal is calculated to second order in the electron-ion potential. The result is evaluated for a number of metals, and shows, generally, a small deviation from the free-electron susceptibility which can be positive or negative. When electron correlations are also taken into account, the theory yields liquid-metal susceptibilities and changes in susceptibility on melting roughly comparable to experiment.

I. INTRODUCTION

CONSIDERABLE effort has been devoted to the calculation of the transport properties of liquid metals, particularly the resistivity, in terms of the liquid-structure factor and the electron-ion pseudopotential.[1,2] This paper presents a calculation of the magnetic susceptibility using the same nearly-free-electron picture.

The approach here is parallel to the work of Glasser[3] and Samoilovich and Rabinovich,[4] who consider the nearly-free-electron susceptibility of solid metals. Their calculations for crystals are easily extended to liquids because they make no particular use of the lattice periodicity. This is in contrast to the more usual treatments of solids (e.g., Ref. 5) which exploit the lattice symmetry.

II. PHYSICAL PICTURE

The motion of the conduction electrons in a liquid metal is described by a one-electron Hamiltonian

$$\mathcal{H}=\mathcal{H}_0+V(\mathbf{r})=\frac{1}{2m}\left(\mathbf{p}-\frac{e}{c}\mathbf{A}\right)^2+\mu H\sigma_z+V(\mathbf{r}). \quad (1)$$

$V(\mathbf{r})$ is the electron-ion potential, $\mathbf{H}=H\hat{z}$ is the magnetic field, $\mathbf{A}=(-Hy,0,0)$ is the vector potential, and $\mu=|e|\hbar/2mc$ is the Bohr magneton. The $\mu H\sigma_z$ term in the Hamiltonian leads to the Pauli spin susceptibility χ_P. The $-(e/c)\mathbf{A}$ term gives the Landau orbital susceptibility χ_L. In the next section we shall keep both of these terms and calculate the effect of the ion potential V on the total electronic susceptibility χ. The results for χ_P and χ_L separately will also be presented. This separation must be made because the correlation corrections for χ_P and χ_L are different, as will be seen in Sec. VI.

The electron-ion potential has the form

$$V(\mathbf{r})=\sum_{i=1}^{N} v(\mathbf{r}-\mathbf{R}_i), \quad (2)$$

where N is the number of ions in the volume Ω and $\mathbf{R}_i$ is the position of the ith ion. It is convenient to work with the Fourier transform

$$V(\mathbf{q})=\int d^3r\, e^{-i\mathbf{q}\cdot\mathbf{r}}V(\mathbf{r})=S(\mathbf{q})v(\mathbf{q})\Omega, \quad (3)$$

where

$$S(\mathbf{q})=\frac{1}{N}\sum_{i=1}^{N} e^{-i\mathbf{q}\cdot\mathbf{R}_i}$$

is the liquid-structure factor, and

$$v(\mathbf{q})=(N/\Omega)\int d^3r\, e^{-i\mathbf{q}\cdot\mathbf{r}}v(\mathbf{r})$$

is the pseudopotential form factor.[6] The results will be applicable to a liquid, crystal, or an amorphous conductor. All the information on the ion distribution is contained in the structure factor $S(\mathbf{q})$.

III. CALCULATION

We begin by calculating the partition function, using the full Hamiltonian [Eq. (1)]:

$$Z(\beta)=\mathrm{Tr}\{e^{-\beta\mathcal{H}}\}=\mathrm{Tr}\{e^{-\beta(\mathcal{H}_0+V)}\}, \quad \beta=1/kT. \quad (4)$$

The essential nearly-free-electron assumption is that V is small. The trace may then be expanded to second order in V using the Schwinger formula[3]

$$Z(\beta)\cong\mathrm{Tr}\{e^{-\beta\mathcal{H}_0}\}-\beta\,\mathrm{Tr}\{V(\mathbf{r})e^{-\beta\mathcal{H}_0}\}+\tfrac{1}{2}\beta^2\,\mathrm{Tr}\left\{\int_0^1 du\, V(\mathbf{r})e^{-\beta\mathcal{H}_0(1-u)}V(\mathbf{r})e^{-\beta\mathcal{H}_0 u}\right\}. \quad (5)$$

The traces are now evaluated using the eigenfunctions of $\mathcal{H}_0$.[7] The procedure for doing the trace integrals is

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[1] J. M. Ziman, Advan. Phys. **16**, 551 (1967).

[2] N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).

[3] M. L. Glasser, Phys. Rev. **134**, A1296 (1964); J. Math. Phys. **5**, 1150 (1964).

[4] A. G. Samoilovich and E. Ya. Rabinovich, Fiz. Tverd. Tela **5**, 778 (1963) [English transl.: Soviet Phys.—Solid State **5**, 576 (1963)].

[5] P. K. Misra and L. M. Roth, Phys. Rev. **177**, 1089 (1969).

[6] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[7] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Co., Reading, Mass., 1965).

outlined in Ref. 3. The resulting second-order partition function is

$$Z(\beta)=\frac{2\Omega\mu H}{\sqrt{\beta}}\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\coth(\beta\mu H)\Bigg\{1-\beta v(0)$$

$$+\tfrac{1}{2}\beta^2\frac{\Omega}{(2\pi)^3}\int d^3q\,|S(\mathbf{q})v(\mathbf{q})|^2\int_0^1 du$$

$$\times\exp[-(q_x^2+q_y^2)\hbar c/|e|HA-q_z^2u(1-u)\beta\hbar^2/2m]\Bigg\}\,, \tag{6}$$

where

$$A=\coth(\beta\mu Hu)+\coth(\beta\mu H(1-u)).$$

We are only interested in the linear response to the applied field. Therefore we can expand the partition function to second order in H.

$$Z(\beta)=\frac{2\Omega}{\beta^{3/2}}\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\Bigg[\left(1+\frac{\beta^2\mu^2H^2}{3}\right)\Bigg(1-\beta v(0)$$

$$+\frac{\beta^2}{2}\frac{\Omega}{(2\pi)^3}\int d^3q\,|S(\mathbf{q})v(\mathbf{q})|^2\int_0^1 dx\,e^{-\beta E(q^2)(1-x^2)/4}\Bigg)$$

$$+\frac{\beta^5\mu^2H^2}{96}\frac{\Omega}{(2\pi)^3}\int d^3q\,|S(\mathbf{q})v(\mathbf{q})|^2E(q_x^2+q_y^2)$$

$$\times\int_0^1 dx\,e^{-\beta E(q^2)(1-x^2)/4}(1-x^2)^2\Bigg], \tag{7}$$

where

$$E(q^2)=\hbar^2q^2/2m.$$

With the partition function we can now calculate the thermodynamic potential per unit volume Φ. The two are related by an inverse Laplace transform[8]:

$$\Phi=\int_0^\infty ds\,\bar{z}(s)\frac{\partial f_0}{\partial s}, \tag{8}$$

where

$$\bar{z}(s)=\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}dt\,e^{st}\frac{Z(t)}{t^2},\quad c>0$$

and f_0 is the Fermi function $f_0=1/(e^{\beta(s-\zeta)}+1)$. For now we make the zero-temperature approximation $\partial f_0/\partial s=-\delta(\zeta)$, ζ being the chemical potential. This will lead to a divergent result at $q=2q_F$, which we shall return to later. Using the δ-function approximation,

$$\Phi=-\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}dt\,e^{\zeta t}\frac{Z(t)}{t^2}. \tag{9}$$

The partition function [Eq. (7)] can be inverted term by term using the theorem[4]

$$\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}dt\frac{e^{xt}}{t^\gamma}=\frac{x^{\gamma-1}}{\Gamma(\gamma)}\theta(x),\quad \gamma>0 \tag{10}$$

where $\Gamma(\gamma)$ is the gamma function and

$$\begin{aligned}\theta(x)&=0,\quad x<0\\ &1,\quad x>0.\end{aligned}$$

When the partition function is inserted in Eq. (9), terms with $\gamma=-\frac{1}{2}$ and $\gamma=-\frac{3}{2}$ result. These are differentiated with respect to ζ until $\gamma>0$. For example,

$$\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}dt\int_0^1 dx\frac{\exp\{t[\zeta-E(1-x^2)/4]}{t^{-1/2}}$$

$$=\frac{\partial}{\partial\zeta}\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}dt\int_0^1 dx\frac{\exp\{t[\zeta-E(1-x^2)/4]\}}{t^{1/2}}.$$

The transform can now be done with Eq. (10), then the x integration and finally the differentiation are performed. The result for the thermodynamic potential is

$$\Phi=\frac{-2}{\sqrt{\pi}}\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\Bigg\{\frac{8}{15}\zeta^{5/2}-\frac{4}{3}v(0)\zeta^{3/2}+\frac{1}{4}\frac{\Omega}{(2\pi)^3}\int d^3q\,|S(\mathbf{q})v(\mathbf{q})|^2E^{1/2}\left(\sqrt{a}+\frac{a-1}{2}\ln\left|\frac{1+\sqrt{a}}{1-\sqrt{a}}\right|\right)$$

$$+\mu^2H^2\Bigg[\frac{2}{3}\zeta^{1/2}-\frac{1}{3}v(0)\zeta^{-1/2}-\frac{2}{3}\frac{\Omega}{(2\pi)^3}\int d^3q\frac{|S(\mathbf{q})v(\mathbf{q})|^2}{E^{3/2}}\frac{1}{a^{1/2}(a-1)}+\frac{1}{4}\frac{\Omega}{(2\pi)^3}$$

$$\times\int d^3q\,|S(\mathbf{q})v(\mathbf{q})|^2\frac{E(q_x^2+q_y^2)}{E^{5/2}}\left(\frac{a^{1/2}(5-3a)}{3(a-1)^2}+\frac{1}{2}\ln\left|\frac{1+\sqrt{a}}{1-\sqrt{a}}\right|\right)\Bigg]\Bigg\}, \tag{11}$$

where $a=4\zeta/E(q^2)$.

The introduction of the potential V shifts the chemical potential ζ away from the Fermi energy ζ_0. This shift may be calculated to second order in V, using the relation $\partial\Phi/\partial\zeta|_{T,\Omega}=-n$, n being the number density of electrons. Differentiating expression (11), and ignoring

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[8] E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) **A210**, 173 (1951).

the field dependence of ζ, we get

$$\zeta=\zeta_0\biggl(1+\frac{v(0)}{\zeta_0}-\frac{1}{4\zeta_0{}^{2/3}}\frac{\Omega}{(2\pi)^3}\times\int d^3q\,\frac{|S(\mathbf{q})v(\mathbf{q})|^2}{\sqrt{E}}\ln\left|\frac{1+\sqrt{a_0}}{1-\sqrt{a_0}}\right|\biggr),\qquad(12)$$

where $a_0=4\zeta_0/E(q^2)$.

The susceptibility is equal to $-(1/H)\partial\Phi/\partial H$. Differentiating expression (11) with respect to H, and using Eq. (12) for ζ, we find the electronic susceptibility

$$\chi=\frac{\mu^2n}{\zeta_0}\biggl(1-\frac{1}{8\zeta_0{}^2}\frac{\Omega}{(2\pi)^3}\int d^3q\,|S(\mathbf{q})v(\mathbf{q})|^2F(\mathbf{q})\biggr),\qquad(13)$$

where

$$F(\mathbf{q})=\frac{a^{1/2}}{2}\ln\left|\frac{1+\sqrt{a_0}}{1-\sqrt{a_0}}\right|+\frac{a_0}{a_0-1}-\frac{q_x{}^2+q_y{}^2}{q^2}\times\biggl(\frac{a_0{}^2(5-3a_0)}{8(a_0-1)^2}+\frac{3}{16}a_0{}^{3/2}\ln\left|\frac{1+\sqrt{a_0}}{1-\sqrt{a_0}}\right|\biggr).$$

Here $\mu^2n/\zeta_0=\chi^0$ is the Landau-Pauli free-electron susceptibility.

Assuming that $v(\mathbf{q})$ depends only on the magnitude of $\mathbf{q}$, the angular integral can be done. The structure factor is replaced by the interference function $I(q)=N|S(\mathbf{q})|^2$, and the integration variable is changed to the dimensionless parameter $k=q/q_F$, q_F being the Fermi wavenumber. The final result for the total electronic susceptibility is

$$\chi=\chi^0(1+\Delta),\qquad(14)$$

where

$$\Delta=-\frac{3}{32}\frac{z}{\zeta_0{}^2}\int_0^\infty dk\,I(k)v^2(k)G(k),$$

$$G(k)=\frac{2}{k}(k^2-1)\ln\left|\frac{k+2}{k-2}\right|+\frac{8}{3}\frac{12+7k^2-3k^4}{(k^2-4)^2}.$$

Here, z is the number of electrons per ion. This is the liquid-metal analog of Glasser's result for the total electronic susceptibility of a solid metal.[3]

The orbital susceptibility may be calculated separately in much the same way. The spin term is omitted from the Hamiltonian; the algebra is much the same:

$$\chi_L=-\tfrac{1}{2}\chi^0(1+\Delta_L),\qquad(15)$$

where

$$\Delta_L=-\frac{3}{32}\frac{z}{\zeta_0{}^2}\int_0^\infty dk\,I(k)v^2(k)G_L(k),$$

$$G_L=\frac{2}{k}(k^2+2)\ln\left|\frac{k+2}{k-2}\right|-\frac{8}{3}\frac{24-22k^2+3k^4}{(k^2-4)^2}.$$

This is the liquid analog of the Misra-Roth nondegenerate calculation of the diamagnetic susceptibility of a crystalline metal.[5]

Finally, keeping only the spin interaction in the Hamiltonian, we get the spin susceptibility

$$\chi_P=\tfrac{3}{2}\chi^0(1+\Delta_P)\qquad(16)$$

where

$$\Delta_P=-\frac{3}{32}\frac{z}{\zeta_0{}^2}\int_0^\infty dk\,I(k)v^2(k)G_P(k),$$

$$G_P(k)=2k\ln\left|\frac{k+2}{k-2}\right|-\frac{8k^2}{k^2-4}.$$

This is the analog of Abe's expression for the paramagnetic susceptibility of a solid, neglecting exchange and correlation.[9]

The analysis would now be complete, except for the fact that the integrands diverge at $k=2$. The logarithm terms and the pole in G_P are integrable as principal values. The quadratic divergences in G and G_L require more effort. In particular, the zero-temperature δ-function approximation has to be modified. The divergent term is the last one in expression (7). When this term in the partition function is inverted to get the corresponding term in the thermodynamic potential, we cannot take $\partial f_0/\partial s=-\delta(\zeta)$. The use of the exact Fermi functions leads to insurmountable mathematical difficulties. Therefore, we have made the physical approximation of letting f_0 drop linearly from 1 to 0 as s ranges from $\zeta-\frac{1}{2}\lambda$ to $\zeta+\frac{1}{2}\lambda$. At the end of the calculation we let $\lambda\rightarrow 0$. This procedure gives the zero temperature result as the limit of a finite temperature:

$$\Phi=\int_0^\infty ds\,\bar{z}(s)\frac{\partial f_0}{\partial s}=-\frac{1}{\lambda}\int_{\zeta-\lambda/2}^{\zeta+\lambda/2}ds\,\bar{z}(s)$$
$$=-\frac{1}{\lambda}\frac{1}{2\pi i}\int_{\zeta-\lambda/2}^{\zeta+\lambda/2}ds\int_{c-i\infty}^{c+i\infty}dt\,e^{st}\frac{Z(t)}{t^2}.\qquad(17)$$

We now insert the last term in Eq. (7) for $Z(t)$, do the s integral, and then the transform. Keeping always the lowest order term in λ, the new result for the quadratic term of $G(k)$ is $8/3(12+7k^2-3k^4)/[(k^2-4)^2-4\lambda^2/\zeta^2]$, which has a well-defined principal value integral at $k=2$. The result is independent of λ as $\lambda\rightarrow 0$.

IV. EVALUATION OF Δ FOR LIQUID METALS

The expressions (14)–(16) for the correction to the susceptibility due to the ion potential have been evaluated for a number of liquid metals.

The interference function is measured by x-ray and neutron scattering. These experiments can be fit with a hard-sphere model of the liquid. The interference functions used here are calculated using the Percus-

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[9] R. Abe, Progr. Theoret, Phys. (Kyoto) **29**, 23 (1963).

TABLE I. Susceptibility corrections for liquid metals.

	Δ	Δ_L	Δ_P
Li	0.32	−0.087	0.18
Na	0.037	−0.024	0.017
K	0.011	−0.012	0.003
Rb	0.007	−0.008	0.002
Cs	0.014	−0.011	0.006
Zn	−0.010	0.047	0.009
Cd	0.040	−0.019	0.020
Hg	0.032	0.040	0.035
Al	−0.019	−0.005	−0.014
In	0.029	0.008	0.022
Pb	0.045	−0.094	−0.002

Yevick theory, according to the procedure outline in Ashcroft and Lekner.[2] The packing density is 0.45 and the sphere radii are taken from the Table in Ref. 2. The pseudopotential form factors used are those of Animalu and Heine, tabled in Harrison.[6] These interference functions and pseudopotentials give a satisfactory account of the resistivity of most liquid metals.[2]

The Δ integrals are evaluated by integrating numerically on either side of $k=2$, coming close enough that the smooth part of the integrand (everything but the divergent factor) does not vary appreciably across the gap. The smooth part is then factored out, and the principal value of the integrand near $k=2$ is calculated analytically. The G functions are of course the same for all metals, but the results vary markedly in magnitude and sign because the different interference functions and pseudopotentials weight different regions of the integrand. All the results come about as subtractions of the contributions from the various regions ($k<2$, $k\approx 2$, $k>2$), and so are rather sensitive to changes in $I(q)$ and $v(q)$.

The results of this calculation for various metals are given in Table I. We see that, in general, the deviation from free-electron behavior is quite small Note that all the deviations can take either sign. For a crystal Δ_L cannot be positive unless by chance a reciprocal-lattice vector is quite close to $k=2$.[5] In contrast, all liquids see the point $k=2$, and if there is enough interference function and pseudopotential there, Δ_L can be positive.

The only other calculation of liquid-metal susceptibility is due to Baltensperger.[10] His calculation of Δ_L is a quadrature over the same types of terms as presented here, but is different. Baltensperger interprets his result as always negative, whereas we believe Δ_L can be positive for some materials. His evaluation of Δ_L for Na is an order of magnitude larger than that given here. We believe that pseudopotentials in current use cannot yield such a large result. The value in Table I is more in line with Δ_L in solids.[5]

V. EVALUATION OF Δ FOR SOLIDS

Now that we have calculated the corrections to the free-electron susceptibility of a liquid due to the potential of the ions, we compute these corrections for solids in the same approximation. Then the difference between the susceptibility of the solid and liquid can be determined and compared with experiment. Expressions for Δ, Δ_L, and Δ_P have been calculated for crystalline metals by Glasser,[3] Misra and Roth,[5] and Abe,[9] respectively:

$$\Delta=-\frac{1}{8\zeta_0{}^2}\sum_k{}' v^2(k)\left(F_1-\frac{k_x{}^2+k_y{}^2}{k^2}F_2\right),$$

$$\Delta_L=-\frac{1}{8\zeta_0{}^2}\sum_k{}' v^2(k)\left(F_1+\frac{k_x{}^2+k_y{}^2}{k^2}2F_2\right),$$

$$\Delta_P=-\frac{1}{8\zeta_0{}^2}\sum_k{}' v^2(k)F_1, \tag{18}$$

$$F_1=\frac{1}{k}\ln\left|\frac{k+2}{k-2}\right|-\frac{4}{k^2-4},$$

$$F_2=\frac{3}{2k^3}\ln\left|\frac{k+2}{k-2}\right|+\frac{2}{k^2}\frac{5k^2-12}{(k^2-4)^2}.$$

Here, k is a reciprocal-lattice vector expressed in units of the Fermi wave number. We have evaluated these expressions for some cubic crystals by summing over the first six reciprocal-lattice vectors, using the same Animalu and Heine pseudopotentials as for the liquids. The results, given in Table II, are of the same order of magnitude as found for liquids.

VI. CORRELATION

Before comparing calculated susceptibilities with experiment, it is necessary to take into account the effect of correlation of the electrons. The correlation correction is larger than the ion-potential correction calculated here. The spin and orbital susceptibilities must be treated separately. This is whay we have calculated Δ_P and Δ_L separately.

Spin susceptibility χ_P. Exchange and correlation are very important in calculating the spin susceptibility.[11]

TABLE II. Susceptibility corrections for solid metals.

	Δ	Δ_L	Δ_P
Li	0.52	−0.36	0.23
Na	0.057	−0.039	0.025
K	0.022	−0.014	0.009
Rb	0.011	−0.005	0.005
Cs	0.018	−0.009	0.009
Al	−0.001	−0.050	−0.018
Pb	0.084	−0.136	0.011

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[10] W. Baltensperger, Phys. Kondensierten Materie **5**, 115 (1966).

[11] C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IV.

TABLE III. Correlation corrections for liquid metals.

	r_s	$\delta_{\mathrm{ex+cor}}$
Li	3.32	−0.23
Na	4.05	−0.24
K	5.02	−0.24
Rb	5.37	−0.24
Cs	5.78	−0.23
Zn	2.33	−0.20
Cd	2.66	−0.21
Hg	2.70	−0.21
Al	2.16	−0.19
In	2.44	−0.20
Pb	2.36	−0.20

An expression for χ_P which is exact in the high-density limit has been calculated by Brueckner and Sawada.[12] A calculation for metallic densities is given by Silverstein.[13] For the densities of interest here ($r_s \approx 4$), these two are essentially the same.[14] Including these exchange and correlation effects the spin susceptibility becomes

$$\chi_P = \tfrac{3}{2}\chi^0 (1 - \Delta_P + \delta_{\mathrm{ex+cor}})^{-1}. \tag{19}$$

$\delta_{\mathrm{ex+cor}}$ can be estimated from the graph in Ref. 13, or computed using the Brueckner and Sawada result: $\delta_{\mathrm{ex+cor}} = -0.166 r_s + 0.204 r_s^2 (0.225 - 0.0676 \ln r_s)$. We have replaced m/m^* in Silverstein's expression with $1 - \Delta_P$, where Δ_P is the effect of the ion potential calculated above. Equation (19) is consistent with Abe's treatment of correlation in χ_P.[9] These corrections are tabulated in Table III. The calculation of the spin susceptibility including the full effect of the electron-electron interaction is a difficult many-body problem, the solution to which these corrections are only crude estimates.

Orbital susceptibility χ_L. The effect of exchange and correlation on the diamagnetic part is less well understood. An estimate by Kanazawa and Matsudaira[15] valid at high density is

$$\chi_L = -\tfrac{1}{2}\chi^0 [1 + 0.028 r_s (\ln r_s + 1.51)].$$

In the limit in which this result is strictly valid ($r_s \ll 1$), this correction is small and negative (for $r_s = 0.1$ the correction is -0.002). It is possible that the true correction remains small at metallic densities, even though the Kanazawa and Matsudaira expression becomes large and positive for $r > 1$ (the correction is 0.12 for $r_s = 2$). For this reason no correlation correction has been made to χ_L in the final results which will be compared with experiment in the next section. However, if the Kanazawa and Matsudaira expression should be approximately correct for metallic densities, the resulting correction to χ_L would be appreciable, generally larger than the ionic correction Δ_L.

VII. COMPARISON WITH EXPERIMENT

The experimental electronic susceptibility listed in Table IV is computed by subtracting the ionic susceptibility[16] from the total measured susceptibility of the metal. The experimental susceptibilities for the alkalies are taken from Collings,[17] the others from the tables of Busch and Yuan.[18] The uncertainty in the experimental susceptibilities is rather large. Measurements of the total susceptibility vary as much as 10%, and the error in the ionic diamagnetism could be 10% or more. The estimates in Table IV are computed assuming both errors are 10%.

Using the relation $\chi_{\mathrm{calc}} = \frac{3}{2}\chi^0 (1 - \Delta_P + \delta_{\mathrm{ex+cor}})^{-1} - \frac{1}{2}\chi^0 (1 + \Delta_L)$ with the values obtained in the preceding sections we obtain the electronic susceptibilities listed in Table IV. The free-electron susceptibilities are computed using the density at $T = 293$°K for the solid and and at the melting point for the liquid.

For the alkalis and the trivalent metals, the calculated susceptibilities are roughly comparable to the experiments. The calculated values fall generally between the free-electron values and the experimental values. Except for Li, the correlation correction is more important than the ion-potential correction in achieving a substantial shift from the free-electron susceptibility.

For the divalent metals and Pb the experimental susceptibility is much smaller than the calculation, smaller even than the free-electron susceptibility. These cannot be understood with the physics considered here.

In principle, the change in the susceptibility at the melting point is a better experimental test of the theory than its magnitude. Experimentally, it should be easier to measure the relative shift in the susceptibility than the absolute value, and the uncertainty in the ionic diamagnetism plays no role in deducing the electronic part. On the theoretical side, the effect of correlation is

TABLE IV. Electronic susceptibilities of solid and liquid metals, cgs units ×10⁶.

		Liquid χ		Solid χ		$\chi_{\mathrm{liq}} - \chi_{\mathrm{sol}}$	
	χ^0	calc	expt	calc	expt	calc	expt
Li	0.52	1.1	1.9 ±0.2	1.3	2.0 ±0.2	−0.2	−0.1
Na	0.43	0.65	0.81±0.08	0.67	0.82±0.08	−0.02	−0.01
K	0.34	0.51	0.69±0.07	0.52	0.70±0.07	−0.01	−0.01
Rb	0.32	0.47	0.65±0.07	0.48	0.68±0.07	−0.01	−0.03
Cs	0.30	0.44	0.82±0.08	0.45	0.87±0.09	−0.01	−0.05
Zn	0.74	1.0	0.37±0.2				
Cd	0.65	0.95	0.40±0.3				
Hg	0.64	0.94	0.18±0.3				
Al	0.80	1.1	1.2 ±0.2	1.1	1.7 ±0.2	−0.05	−0.5
In	0.71	1.0	0.70±0.1				
Pb	0.73	1.0	0.54±0.2	1.1	0.22±0.1	−0.06	+0.3

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[12] K. A. Brueckner and K. Sawada, Phys. Rev. **112**, 328 (1958).

[13] S. D. Silverstein, Phys. Rev. **130**, 1703 (1963).

[14] See graph Ref. 11, p. 66.

[15] H. Kanazawa and N. Matsudaira, Progr. Theoret. Phys. (Kyoto) **23**, 433 (1960).

[16] P. W. Selwood, *Magnetochemistry* (Wiley-Interscience, Inc., New York, 1956).

[17] E. W. Collings, Phys. Kondensierten Materie **3**, 335 (1965).

[18] G. Busch and S. Yuan, Phys. Kondensierten Materie **1**, 37 (1963).

quite small, at least in the Silverstein approximation. The principal contribution to the shift comes from Δ_P and Δ_L, with the change in χ^0 caused by the change in density somewhat smaller. The unfavorable aspect of the susceptibility shift is that it is quite small. Again excepting Pb, the theory predicts the correct sign for the shift, and for some metals gives a fair account of its magnitude. It should be emphasized again that the error in the experimental results is quite large.

The qualitative agreement with experiment for the alkalis and the trivalent metals indicates that the basic physical picture considered here is an adeuqate one for these materials. The metal is represented by a distribution of point ions, immersed in a sea of interacting electrons. Perhaps the calculated susceptibilities could be brought closer to the experiments by a better treatment of the electron-electron interaction which both correlates the spins and screens the ion potential.

The theory does not seem to work for the divalent metals. The experimental susceptibility above the melting point is much smaller than the free-electron value and strongly temperature-dependent.[19] There is evidence from the Knight shift in Cd that χ_P takes the free-electron value and is temperature-independent.[20] Some new physics, probably involving the d electrons, will be needed to understand the susecptibility of these liquids.

VIII. CONCLUSIONS

The objective of the investigation has been to calculate the effect of the ion potentials on the susceptibility of liquid metals in terms of the liquid-structure factor and the ion pseudopotential. This correction turns out to be small and can be of either sign. When correlation of the electron spins is taken into account, a larger effect than the ion-potential corrections, the calculated susceptibilities are in rough agreement with experiment for some simple metals. Estimates of the shift in susceptibility on melting also are roughly confirmed by experiment.

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Energy Bands for fcc Lanthanum and Praseodymium†

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We have calculated the energy bands of lanthanum and praseodymium in the face-centered-cubic structure using the relativistic augmented-plane-wave method. Calculations for the density of states, the magnetic susceptibility, and the Fermi surface are also performed, and the results are correlated with some of the electronic and magnetic properties of these metals.

LIGHT rare earths La ($Z=57$), Pr ($Z=59$), and Nd ($Z=60$) can be stabilized in two crystal structures, namely, double hexagonal close-packed (dhcp) and face-centered cubic (fcc).[1,2] Both phases of La are superconducting at sufficiently low temperatures with slightly different superconducting and normal state parameters.[1] Pr and Nd in the dhcp phase order antiferromagnetically at low temperatures, while in the fcc phase, they order ferromagnetically.[2,3] In this paper, we report results of the band calculation of fcc La and Pr and compare them with similar calculations for these metals in the dhcp phase.[4] It will be shown that the differences in superconducting or magnetic properties between the two phases can be understood from the differences in their band structures.

The relativistic augmented-plane-wave (RAPW) method is used for the band calculation.[5,6] The muffin-tin potential is constructed in the standard way from the atomic electron charge density.[7] The Slater $\rho^{1/3}$ exchange energy is assumed. The electronic configuration used for La is $5d^16s^2$ and is $5d^06s^2$ for Pr. The lattice parameters are $a=10.011$ a.u.[8] (5.296 Å) for La and 9.804[2] a.u. (5.186 Å) for Pr. The lattice parameter for fcc Nd has not been determined. The radius of the muffin-tin potential is chosen as 3.158 a.u. The relativistic analog of the logarithmic derivative of the wave function is found to be divergent in the energy

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