TABLE I. Experimentally determined parameters.

Alloy conc	Belly radius (mrad)	Neck radius (mrad)	Peak coincidence (counts/point)
90/10	5.35	1.0	42 000
50/50	5.2	1.0	30 000
10/90	4.95	1.0	5 700

in the relative concentration of the constituents. As the percentage of nickel increases, the belly radius decreases. This is to be expected from the fact that the number of conduction electrons is decreasing as nickel atoms are substituted for copper atoms. The values for various dimensions of the Fermi surface are shown in Table I.

The lack of a sharp discontinuity in the slope of the angular-correlation curves at the Fermi momentum has been observed by others in other metals. The smearing at the expected Fermi momentum has been variously attributed to breakdown of the free-electron behávior near the zone boundary,[13] to a broadening of the wave number in an alloy,[14] and to the existence of annihilations with high-momentum components due to conduction electrons in the second zone.[11] Our data do not give any new information on the cause of the smearing as we did not concentrate on the region around the Fermi momentum.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Magnetic Susceptibility of Alkali Metals*

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The magnetic susceptibility of alkali metals is evaluated by a systematic development of the grand partition function for small magnetic fields. The results are expressed in powers of r_s (the interparticle spacing divided by the Bohr radius) and compared with recent experimental and theoretical results. The evaluation is made to order r_s^2, improving the previous calculations. The polarization parameter, which has been used in the previous evaluation of the paramagnetic susceptibility as an adjustable parameter, is not used. Comparison of our results with the recent experiment by Collings is satisfactory.

I. INTRODUCTION

Recently we have considered the effects of Coulomb interactions on the diamagnetic susceptibility of an electron gas. We found at high temperatures a small increase in the susceptibility that is proportional to the plasma parameter[1] and at low temperatures a much larger increase due to an exchange effect.[2] A similar increase in the diamagnetic susceptibility has been observed by March and Donovan and by Kanazawa and Matsudaira.[3]

In this paper we shall extend our previous consideration to the evaluation of the paramagnetic susceptibility. The feature of our calculation is in the use of a propagator method: We shall calculate the grand partition function in powers of $a^2 = eH/c$ taking into consideration the ring and exchange graphs. The total magnetic susceptibility is given at once by the grand partition function. The paramagnetic part can be separated out from the diamagnetic part by picking up all terms involving Landé's g factor. That is, we shall evaluate the grand partition function for an arbitrary g. Therefore, our method is completely statistical mechanical in comparison with related theories to be discussed later.[3–9] This method enables us to evaluate both the paramagnetic and diamagnetic susceptibilities at the same time. Our results on the diamagnetic susceptibility improve the previous results since the evaluation is made to order r_s^2. r_s is the interparticle spacing divided by the Bohr radius. The paramagnetic susceptibility shall be evaluated without the polarization parameter used in the previous theories as an adjustable parameter.

Comparison of our results with experiments requires the effective mass of the electrons. While there are several choices, we have used the effective mass determined from the specific heat. Since this effective mass is completely free from our steps for the susceptibility, the choice seems to be advantageous. Comparison with experiments shows that our results evaluated from first principles are satisfactory.

II. SUSCEPTIBILITY

We shall adopt in this paper the units such that $\hbar = 1$ and $2m = 1$. The susceptibility is given by

$$\chi = \frac{1}{V\beta H}\left(\frac{\partial \ln \Xi}{\partial H}\right)_{V,T,z}, \tag{2.1}$$

where V is the volume, $\beta = 1/kT$, H is the magnetic field, Ξ is the grand partition function, and z is the absolute activity. In the ring diagram approximation the grand partition function is given by

$$\ln\left(\frac{\Xi}{\Xi_0}\right) = \left(\frac{1}{2\pi}\right)^3 \frac{V}{2}\int d\vec{q} \sum_{\vec{k}} \{u(q)\lambda_k(q) - \ln[1 + u(q)\lambda_k(q)]\}, \tag{2.2}$$

where Ξ_0 is the grand partition function in the absence of interaction, $u(q)$ is the Fourier transform of the Coulomb interaction, and[2]

$$\lambda_k(q) = \left(\frac{1}{2\pi}\right)^3 \sum_{l=1}^{\infty} \sum_{j=0}^{l-1} (-)^{l+1} z^l \left(\frac{\pi^3}{l\beta}\right)^{1/2} \frac{2a^2 \cosh gl\beta a^2/2}{\sinh l\beta a^2} \times \int_0^\beta d\alpha \exp\left[\frac{2\pi i k\alpha}{\beta} - q_z^2(j\beta+\alpha)\left(1 - \frac{(j\beta+\alpha)}{l\beta}\right) - (q_x^2 + q_y^2)\frac{\sinh(j\beta+\alpha)\sinh[(l-j)\beta-\alpha]a^2}{a^2 \sinh l\beta a^2}\right]. \tag{2.3}$$

In the absence of the magnetic field H this eigenvalue reduces to the correct limiting expression. In the small-q approximation it is

$$\lambda_k^{(0)}(q) = \frac{p_F}{2\pi^2}(1 - u \tan^{-1} u^{-1}) \equiv \frac{p_F}{2\pi^2} R(u), \tag{2.4}$$

where if q_z is the momentum in the direction of the magnetic field then

$$u = \pi k/\beta p_F q_z. \tag{2.5}$$

For a finite magnetic field one can expand $\lambda_k(q)$ in powers of $a^2 = eH/c$,

$$\lambda_k(q) = \lambda_k^{(0)}(q) + a^4 \lambda_k^{(1)}(q) + O(a^8); \tag{2.6}$$

for the purpose of evaluating the susceptibility, terms higher than a^4 are not needed.

The grand partition function given by Eq. (2. 2) is not sufficiently accurate, as in the case of the evaluation of the correlation energy: One needs to take exchange graphs into consideration. Then the first term $u(q)\lambda_k(q)$ in the integrand of Eq. (2. 2) becomes $u(q)D(q)$, where

$$D(q) = \frac{\beta a^2}{4\pi^{3/2}} \sum_{l=1}^{\infty} (-)^{l+1} z^l \left(\frac{1}{l\beta}\right)^{1/2} \frac{\cosh gl\beta a^2/2}{\sinh l\beta a^2}. \tag{2.7}$$

As Eq. (2. 6) this can be expanded in powers of a^2,

$$D(q) = D^{(0)}(q) + a^4 D^{(1)}(q). \tag{2.8}$$

As a result, the grand partition function becomes

$$\ln \Xi_{x+r} = \frac{Ve^2}{8\pi^2\beta}\left(\frac{2\eta^2}{\pi}\right) - \frac{V\beta e^4 p_F^3 \phi(2)}{2\pi^5}\left(\ln\frac{2e^2}{\pi p_F} + \frac{\phi'(2)}{\phi(2)} - \frac{1}{2}\right) + \frac{V\beta a^4}{16\pi^3}\left[e^2\left(g^2 - \frac{10}{9}\right) - \frac{e^2}{9}\ln\frac{e^2}{2\pi p_F} - \frac{e^4}{18\pi p_F} - \frac{4e^4}{\pi^2 p_F}\left(\frac{g^2}{4} - \frac{1}{3}\right) \times \left(\ln\frac{2e^2}{\pi p_F}\int_0^\infty du\, G(u)R(u) + \int_0^\infty du\, G(u)R(u)\ln R(u)\right)\right] + O(e^6), \tag{2.9}$$

where

$$\phi(2)=\tfrac{1}{3}\pi(1-\ln 2),$$

$$\phi'(2)=\int_0^\infty du\, R^2(u)\ln R(u), \tag{2.10}$$

$$G(u)=(u^2-1)/(1+u^2)^2 .$$

From this result one finds the susceptibility as follows:

$$\chi=\chi_d+\chi_p, \tag{2.11}$$

$$\chi_d=\chi_d^{(0)}\left[1+\frac{2\alpha r_s}{3\pi}+\frac{\alpha r_s}{6\pi}\ln\frac{\alpha r_s}{\pi}+\frac{(\alpha r_s)^2}{3\pi^2}+\frac{3\phi(2)(\alpha r_s)^2}{\pi^2}\left(\ln\frac{4\alpha r_s}{\pi}+\frac{\phi'(2)}{\phi(2)}-\frac{5}{6}-\frac{\pi}{3}\right)-\frac{4(\alpha r_s)^2}{\pi^3}\right.$$
$$\left.\times\left(\ln\frac{4\alpha r_s}{\pi}\int_0^\infty du\, G(u)R(u)+\int_0^\infty du\, G(u)R(u)\ln R(u)\right)+O(\alpha^3 r_s^3)\right], \tag{2.12}$$

$$\chi_p=\chi_p^{(0)}\left[1+\frac{\alpha r_s}{\pi}+\frac{3\phi(2)(\alpha r_s)^2}{\pi^2}\left(\ln\frac{4\alpha r_s}{\pi}+\frac{\phi'(2)}{\phi(2)}-\frac{5}{6}-\frac{\pi}{3}\right)\right.$$
$$\left.-\frac{4(\alpha r_s)^2}{\pi^3}\left(\ln\frac{4\alpha r_s}{\pi}\int_0^\infty du\, G(u)R(u)+\int_0^\infty du\, G(u)R(u)\ln R(u)\right)+O(\alpha^3 r_s^3)\right]. \tag{2.13}$$

The integrals and constants appearing in these results are

$$\alpha=(4/9\pi)^{1/3},$$
$$\phi(2)=0.3213,$$
$$\phi'(2)/\phi(2)=-0.5511, \tag{2.14}$$
$$\int_0^\infty du\, G(u)R(u)=-0.6961,$$
$$\int_0^\infty du\, G(u)R(u)\ln R(u)=0.0717.$$

Introducing these numbers, we arrive at our final results:

$$\chi_p^*=(2.5882/r_s)(m^*/m)+0.4289-0.2265 r_s+0.1312 r_s\ln r_s+O(r_s^2), \tag{2.15}$$

$$-\chi_d^*=(0.8627/r_s)(m/m^*)+0.0525+0.0238\ln r_s-0.0677 r_s+0.0437 r_s\ln r_s+O(r_s^3), \tag{2.16}$$

where the asterisk indicates that an effective mass m^* of electrons has been introduced.

III. DISCUSSION

To compare our results with experiments it is necessary to know the effective mass of electrons. While there are different ways of determining the effective mass, we list in Table I those determined from the specific heat at low temperatures. From the electronic specific-heat constant γ, one obtains

$$m^*/m=\gamma_{\text{exp}}/\gamma_{\text{free}}, \tag{3.1}$$

where

$$\gamma_{\text{free}}=\pi^2k^2N_0/2\epsilon_F . \tag{3.2}$$

Here N_0 is Avogadro's number.

The effective masses in Table I are experimental and differ from those determined by some other methods.[4] It is worthwhile to use these effective masses in the susceptibility results because they are accurately determined, completely independent of theoretical assumptions and of the susceptibility. In Table II we have listed our final results on the paramagnetic susceptibility and compared them with experimental results and the values predicted by Pines and Silverstein.[4,8] The experiment values are due to the recent paper by Collings.[5]

In obtaining the values in Table II, Pines considered the energy change due to the variation in the population of electrons of different spins in the way Sampson and Seitz did. He improved the calculation greatly with a more reliable correlation energy than that employed by Sampson and Seitz.[6] The susceptibility is obtained in terms of the polarization parameter thus determined. In the determination a

TABLE I. Effective mass of electrons in alkali metals.

	Li	Na	K	Rb	Cs
ϵ_F(eV)[a]	4.7	3.1	2.1	1.8	1.5
γ_{free}(μcal/°K mole)	179.89	272.73	402.61	469.71	563.65
γ_{expt}(μcal/°K mole)[b]	390 ± 4	330 ± 5	497 ± 20	576^{+70}_{-40}	764 ± 250
m^*/m	2.168	1.210	1.234	1.226	1.355

[a] C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1966).

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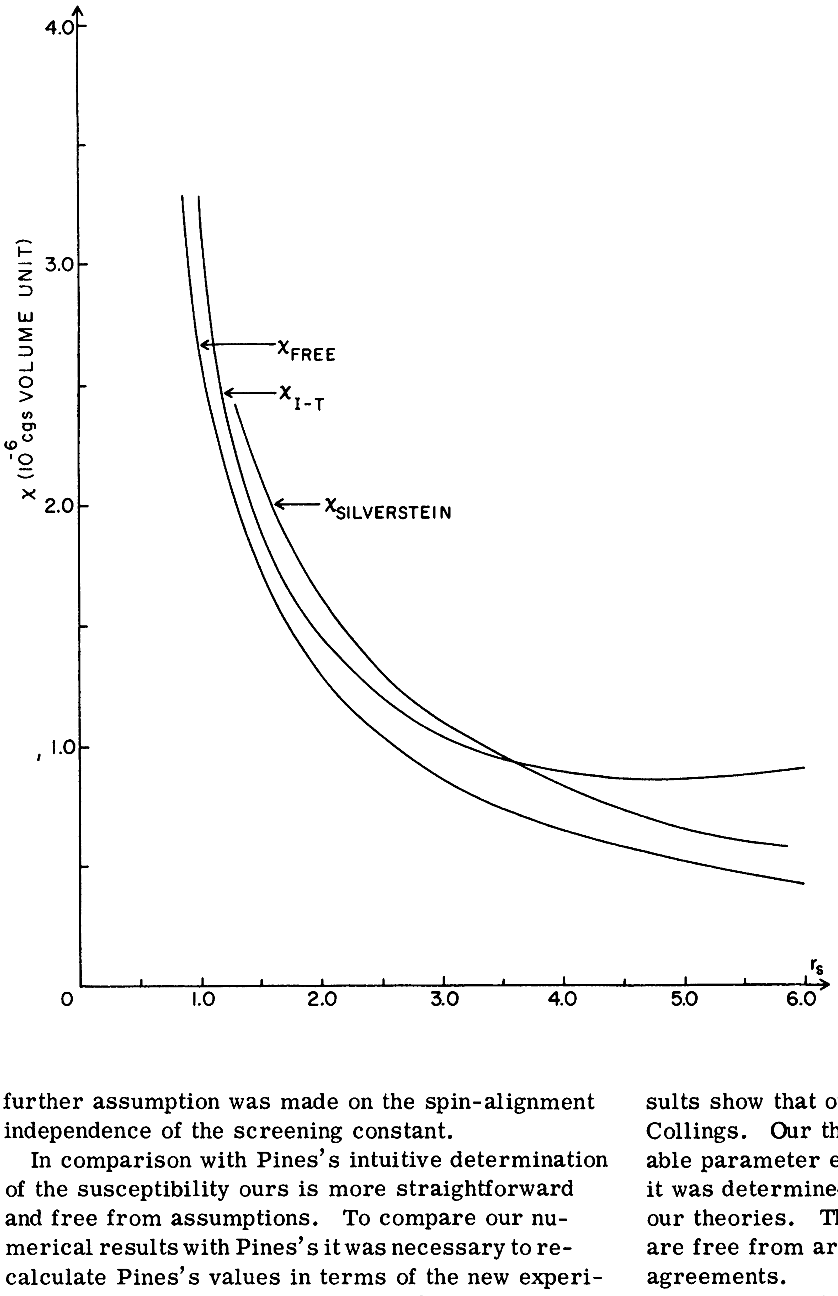

FIG. 1. Paramagnetic susceptibility as a function of r_s for $m^*=m$.

further assumption was made on the spin-alignment independence of the screening constant.

In comparison with Pines's intuitive determination of the susceptibility ours is more straightforward and free from assumptions. To compare our numerical results with Pines's it was necessary to recalculate Pines's values in terms of the new experimental effective masses which we adopted. The results show that our values are closer to the data by Collings. Our theory does not include any adjustable parameter except for the effective mass, but it was determined independently of both Pines's and our theories. Therefore, the results in Table II are free from artificial adjustment to achieve closer agreements.

The theory of Pines has been further pursued by

TABLE II. Susceptibility of alkali metals ($\times 10^6$ cgs volume units).

		Li	Na	K	Rb	Cs
	r_s	3.22	3.96	4.87	5.18	5.57
	ρ(g/cm^3)	0.53	0.97	0.85	1.48	1.89
Expt (Collings)	χ_{ion}	−0.053	−0.291	−0.372	−0.398	−0.487
	χ_d^*	−0.150	−0.235	−0.241	−0.249	−0.249
Theory (Ishihara and Tsai)	χ_p^*	1.936	1.038	0.993	0.986	1.052
	χ_{tot}^*	1.773	0.511	0.380	0.339	0.316
Theory (Pines and Silverstein)	χ_{tot}^*	1.95	0.43	0.21	0.25	0.52
Expt (Collings)	χ_{tot}^*	1.789	0.583	0.389	0.310	0.398

$\chi_{\text{tot}} = \chi_p + \chi_d + \chi_{\text{ion}}$

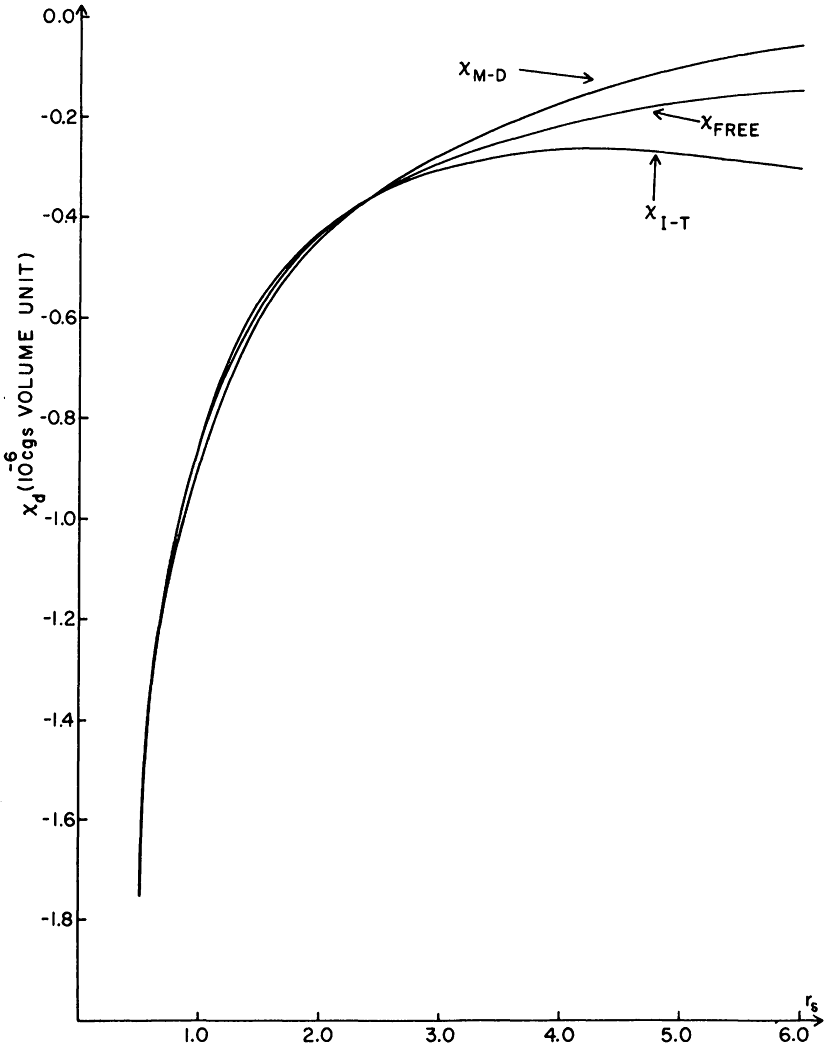

FIG. 2. Diamagnetic susceptibility as a function of r_s for $m^* = m$.

Shimizu.[7] Independently, Silverstein[8] obtained the spin susceptibility using the theory of Brueckner and Sawada.[9] These two theories are both based on random-phase approximation (RPA) but differ from each other in detail. For instance, for small q the spin stiffness expansion differs in the second term due mainly to the dubious assumption made by Shimizu concerning the independence of the summed series of spin polarization. Further differences appear in higher-q terms because while Shimizu considered the second-order exchange terms Silverstein used only the second-order nonexchange perturbation for antiparallel spin configurations. While our calculation is closer to Silverstein's than Shimizu's, there are several important differences. First, we have not used the polarization parameter P used by these authors but rather evaluated the parameter from the grand partition function. Second, we have included the exchange interaction and improved the RPA calculation by expanding the eigenvalues in powers of a^2 rather than P^2. The polarization parameter can be determined as a function of a^2 and r_s from our grand partition function. It is not an adjustable parameter.

For explicit results, Silverstein took into consideration the effects of the lattice by using the lattice effective mass in the kinetic energy. Because the electrons in the immediate vicinity of the Fermi surface contribute to the susceptibility, effective masses based on a band theory were adopted. These effective masses are different from those determined from the specific heat which is also due to the electrons at the Fermi surface. The specific-heat effective mass can be ascribed to various sources such as band structure and electron-phonon interactions. The importance of electron-phonon interactions has been stressed by Ashcroft and Wilkins,[10] and the considerations only of the band-structure corrections by Shimizu and Silverstein seem not to be sufficient. Moreover, judging from the recent data of Collings, the paramagnetic susceptibilities for Li and Na can be much less than those used by Silverstein for comparison. Since all theoretical results depend on effective mass a precise comparison of theoretical results is difficult. However, in Fig. 1, we have compared our result on the paramagnetic susceptibility with Silverstein's.

In our numerical results we have chosen $g = 2$, but our theoretical formulas were derived for arbitrary g. In the past several years, accurate measurements of the electron g value have been made by conduction electron-spin resonance.[11] For alkali metals it has been found that g value is very nearly that of the free electron. The largest difference of 1.07×10^{-2} has been found for He while in Li the difference is $(-2\pm2)\times10^{-6}$.

The diamagnetic susceptibility reported by Kanazawa and Matsudaira needs two corrections. First, in their notation the correct ratio of the susceptibility to that of an ideal electron gas is

$$\frac{\chi}{\chi_0} = 1 + \frac{\alpha r_s}{6\pi}\left(\ln r_s + 4 + \ln\frac{\alpha}{\pi}\right).$$

The extra term $\ln\frac{1}{2}$ appearing in the bracket in their result is due to the effect of spin missing in their expression for the screening constant. Second, their numerical value 1.12 is correctly 0.86. This value is then not close to that which March and Donovan obtained, i.e., 1.51.

Figure 2 illustrates our results on the diamagnetic susceptibility in comparison with that of free-electron gas and also March and Donovan. The theoretical susceptibility curves for an interaction-electron gas cross with that of free electrons at $r_s = 2.75$ and the deviation becomes larger for larger r_s as expected. Our result (2.12) improves what Kanzawa and Matsudaira reported. It gives terms to the second order in r_s.

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Exchange Core-Polarization Contribution to the Spin Density in Liquid Metals

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A theory is developed for the exchange core-polarization (ECP) contribution to spin density S^{cp} in liquid metals in the framework of moment-perturbation (MP) procedure and pseudopotentials. The zero-order contribution to S^{cp} has been shown to be temperature independent while the first-order term depends on the temperature through the liquid-interference function. The results give a definite trend for convergence of the perturbation theory. In the specific case of liquid Mg the ECP contribution to the Knight shift K_s^{cp} is about 25% of the direct shift K_s^d and varies rather slowly with temperature in comparison to that of K_s^d. From the present results it seems that the Fermi-contact term is the most dominant term and determines the major change of the Knight shift with temperature in agreement with what has been predicted previously.

I. INTRODUCTION

Recently Rossini and Knight[1] have investigated a number of liquid metals to understand the various contributions to the Knight shift K_s and nuclear-spin relaxation rate, but in the absence of any theory