Volume dependence of the Pauli susceptibility and the amplitude of the wave functions for Li and Na

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The conduction-electron spin susceptibility χ_P for Li and Na was measured as a function of pressure. By combining the present data with the previously measured volume dependence of the Knight shift of these metals, the volume dependence of the amplitude of the electron wave functions at the nucleus, $P_F(V)$, is deduced for the first time. A comparison with theoretical predictions of $P_F(V)$ for Na indicates that they all agree qualitatively and some agree numerically with the experimentally obtained results. None of the theories, however, correctly predict the experimental results for Li. The Pauli susceptibility enhancement χ_P/χ_F for a jellium model has been a favorite topic among many-body theoreticians. (Here χ_F is the free-electron gas susceptibility.) Dozens of theories of χ_P/χ_F as a function of the Wigner-Seitz radius r_S have been published since 1929. The attempts to compare the theories with experiments made one realize that an important link was missing; the effect of the band structure in real metals on the many-body enhanced susceptibility was not known. The present data for χ_P/χ_F and $d(\chi_P/\chi_F)/dr_S$ for Li support the validity of the newly developed general theory of susceptibility by Vosko and Perdew which incorporates the band-structure effect in a logical way rather than in an *ad hoc* fashion. The perfect agreement between the present data and their calculation of χ_P/χ_F and its derivative for Na strongly supports some of the jellium theories previously proposed.

I. INTRODUCTION

We measured the conduction-electron spin susceptibility χ_P of Li and Na metal as a function of hydrostatic pressure.[1,2] The purpose of this experiment was twofold: (i) to derive the amplitude of the electron wave functions at the nucleus, $\langle |\psi(0)|^2 \rangle$, as a function of volume and compare the results with theoretical predictions [the volume dependence of $\langle |\psi(0)|^2 \rangle$, which is designated as P_F, was thus determined experimentally for the first time]; (ii) to obtain the susceptibility enhancement factor as a function of interelectronic distance directly. We wish to give a decisive experimental answer to a longstanding many-body effect problem in an electron liquid with metallic density.

One of the outstanding theoretical problems[3] in basic metal physics is how to treat an exchange-correlation (XC) effect. There has been little conclusive experimental evidence to demonstrate that one theory is significantly better than the others. A theory of the XC effect, mostly dealing with jellium, has to be tested by comparing it with experimental results for real metals which are not jellium. It is important to choose a phenomenon which exhibits the XC effect prominently, and to select the materials which are the closest replicas of jellium.

Precise band-structure information[3] is another problem which has to be calculated on a first-principles basis and checked against experimental results. The precise knowledge of the wave function has not been well substantiated by experiment even for simple metals such as alkali metals.

One would expect a significant improvement in the understanding of the basic properties of interacting electrons in solids only if (a) reliable band-structure parameters are evaluated and checked by the pertinent experiments, (b) the band-structure effect is incorporated in a logical way, rather than in an *ad hoc* fashion, into the many-body calculation of the XC effect, and (c) the results are compared with clear-cut experiments.

Up to now, there has been a great emphasis on the calculation of energy bands, but very little attention has been given to the electronic wave functions. This is understandable since abundant and detailed experimental information on the Fermi surfaces is available to be compared with the calculated eigenvalues $\epsilon_{\vec{k}}$. However, direct experimentally obtained knowledge of the wave functions is scarce.

Most of the experimental information of $\epsilon_{\vec{k}}$ has been obtained using de Haas–van Alphen (dHvA) type experiments, their modifications, and the anomalous skin effect. These experiments usually require high-purity materials and/or high magnetic field at low temperature, which imposes some restriction on the samples to be studied. Nevertheless, many detailed studies have been published on the experiments and the theoretical calculations of $\epsilon_{\vec{k}}$ in many metals.

It is obvious, however, that the knowledge of the wave functions is as important as that of their eigenvalues to the basic understanding of metal physics. Since the pseudopotential method[4] has become popular, it has been noted that $\epsilon_{\vec{k}}$ is not sensitive to the choice of the potential in a one-electron Schrödinger equation. It is quite pos-

sible that the pseudopotential which reproduces the experimentally observed $\epsilon_{\vec{k}}$ satisfactorily might give poor wave functions.[5] The success and the great popularity of the pseudopotential method are based on the insensitivity of the energy bands to the crystal potential.[6] There seems to be no exact evidence that the pseudopotential method gives numerically correct wave functions.[7]

As numerous calculations[5,8-12] have shown, the wave function, particularly the nuclear contact density $\langle | \psi_{\vec{k}}(0) |^2 \rangle$ $(\equiv P_F)$, is much more difficult to evaluate, since the P_F value critically depends on the choice of the crystal potential. A comparison with the experimentally observed value of P_F is, therefore, a much more critical test for the theory of the electronic states in metals. Unfortunately, reliable experimental values for P_F are available for only a few metals. Even if one can find the experimental P_F value, P_F is a single averaged quantity of $| \psi_{\vec{k}}(0) |^2$ over the Fermi surface. The agreement with the calculation could easily be due to a fortuitious accident. The chance of coincidence is much less in the case of the eigenvalues, where detailed comparisons with experiments are possible.

It is, therefore, important to increase the amount of the experimentally obtained information of P_F for the pertinent metal. The conventional, and the most popular, method is to make alloys with other elements and to study the change of P_F as a function of concentration (metallurgical approach). Another method is to compare the properties related to P_F with those of metallic elements in the same or neighboring column of a periodic table (chemical approach). A great deal of the knowledge of P_F of metals has been accumulated by these approaches. Any interpretation based on these methods, however, inevitably requires additional assumptions, some reasonable and some dubious.

The volume-dependence measurement of P_F is one of the most clear-cut ways to increase the information on the wave functions in metals. The product of P_F and χ_P (in cgs volume units) is obtained experimentally as the Knight shift K for the simple metals,

$$K = \tfrac{8}{3} \pi \chi_P \Omega P_F , \qquad (1)$$

where Ω is an atomic volume.[13]

We have noticed that some authors who are interested in the calculations of P_F assume a crude estimate for χ_P (even a free-electron value) when they compare their results with the experimental values. Other authors, who have a profound knowledge of an idealized metal, tend to compare their calculated χ_P with the experimental K values, making little effort to check the validity of the P_F values obtained by the band-calculation specialists.

It is our impression that the reliability of the theoretical estimate of P_F is not any better than that of χ_P.

The volume dependence of K for alkali metals was measured some time ago.[14] Since then it has been realized that the volume dependence of χ_P deviates considerably from the corresponding free-electron values.[15]

In this paper we describe the first experiment in which the volume dependence of χ_P was measured. From our results we could deduce the volume dependence of P_F experimentally and compare it with the theoretical predictions published previously. The $d\chi_P/dV$ measurement gives one of the most direct experimental checks of the many-body effect at metallic density.

Most of the solid-state problems have been interpreted in terms of the one-electron approximation,

$$[- (\hbar^2/2m)\nabla^2 + V_{ef}]\psi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}} \psi_{\vec{k}}(\vec{r}) . \qquad (2)$$

The effective potential V_{ef} represents the interaction between the electrons and the core ions as well as some of the interaction between the conduction electrons themselves. The simplest V_{ef} is a boxlike potential (Sommerfeld model), which replaces the positive-charge effects of the core ions by an averaged uniform positive-charge distribution. It is surprising that such a simple model with a minor modification explains the gross properties of the metals. This is one of the motivations for the recent development of the pseudopotential theory. The Hartree and the Hartree-Fock potential are well-known forms of the V_{ef}.

The effects which cannot be described by the one-electron model are called, somewhat loosely, many-body effects. The many-body problem has been a most difficult and challenging subject for theoreticians. Most often, this electron-electron interaction has been studied by the theorists in a fictitious metal where the crystalline effect is replaced by a uniform charge distribution; this is the equivalent of the Sommerfeld model for the band-structure calculation. As mentioned above, this idealized metal is commonly called "jellium" or a Fermi liquid. Besides the theoretical difficulties, there are few experimentally accessible quantities which can be compared with the theoretical results directly. Many theories have to base their validity check on self-consistency theorems such as sum rules and/or a fluctuation-dissipation theorem. These rules and theorems are, however, necessary but not sufficient conditions. Experimentally many phenomena are affected to some degree by many-body effects. The results of the effects are usually too subtle to enable one to single out any one theory as the correct one. For

example, the effective mass of alkali metals derived from cyclotron resonance or from the low-temperature specific heat is known to be different from the band-structure effective mass m_B^* by (20–30)%. The observed effective mass consists of three components: m_B^*, the electron-electron enhancement, and an electron-phonon enhancement.[16] There is, however, no known way to separate these three in alkali metals.

The conduction-electron spin susceptibility is one of the exceptions.[17] The enhancement due to the electron-electron interaction is large. It is believed to be 50% or more in jellium at metallic density. The electron-phonon interaction does not affect χ_P in first order.[10,11,18–27] The spin susceptibility is, therefore, one of the most appropriate experimental parameters to study the XC effect.

At the high-density limit, $r_s \ll 1$, where r_s is the Wigner-Seitz radius measured in Bohr units, the problem has been well settled by a random-phase-approximation (RPA) theory.[28–30] In the real-metal range, $2 \lesssim r_s \lesssim 6$, the electron many-body problem has thus far resisted attacks,[31] although many promising attempts have been made. Historically, Bloch[32] first pointed out almost a half century ago that χ_P becomes infinite at $r_s \sim 6$, if one uses the Hartree-Fock (HF) approximation.

The exchange interaction in the HF scheme tends to align the parallel spins. Since the exchange energy ($\propto r_s^{-1}$) becomes more important than the kinetic energy ($\propto r_s^{-2}$) at lower density, the HF electron system becomes magnetically unstable at the low end of the metallic density. Since no such tendency is observed in Cs ($r_s = 5.6$), the correlation effect, which is neglected in the HF approximation and which tends to increase anti-parallel spin alignment, is strongly suppressing the χ_P enhancement in the low-density region.

In the middle metallic range ($r_s \sim 4$), direct measurements of χ_P[1,2,33–35] of Na and K give the most reliable enhancement factor χ_P/χ_F, where χ_F is the susceptibility for a noninteracting electron gas; $\chi_F = 2.589\, r_s^{-1} \times 10^{-6}$ cgs volume units. Since it is generally considered that Na and K are almost a jellium, by combining the exact RPA solution at the high-density limit and these experimental values, we feel that the general trend of the enhancement is understood reasonably well in the region $0 < r_s \lesssim 4$.

At the low metallic range $5 < r_s < 6$, however, neither the experimental nor the theoretical situation was clear at all. There are numerous and diversified theoretical predictions. Some of them predict that χ_P/χ_F keeps increasing as r_s increases, which is similar to the HF result.[32] The others predict that the curve is going to flatten off or bend down. A phase change of jellium has

also been suggested.[36] The Fermi energy of jellium, $2.21/r_s^2$ Ry, becomes comparable to the zero-point energy of plasmons at $r_s \sim 4.5$. Other types of phase changes or an instability before the electron liquid finally (and presumably) freezes to a Wigner lattice at large r_s have been proposed by many authors.[37,38] Wiser and Cohen[39] considered a mechanical ($r_s \gtrsim 5$), a magnetic ($r_s \gtrsim 6$), and a thermodynamical ($r_s \gtrsim 4$) instability of jellium. The magnetic alignment (ferro or antiferro) of the Wigner lattice is discussed by Herring.[40]

Since χ_P is generally a function of q, there is a possibility that $\chi_P(q)_{q \neq 0}$ becomes unstable before the onset of the instability of the static susceptibility $\chi_P(0)$. The possibility of such instability which leads to a spin-density wave in jellium has been an outstanding controversy.[41]

The measurement of χ_P of degenerate semiconductors[42–44] helped little in the understanding of low-density jellium, since the band-structure effect becomes more important relative to the electron interaction. It is a risky step to extrapolate the high- and medium-density jellium to the Wigner lattice state.[45,46]

The measurement of χ_P for Rb and Cs using a spin-wave method seems to be promising. The observed values have, however, a large uncertainty at present.[47] The χ_P values for these metals obtained from the dHvA effect are not unique, since their experimental values give cosines of the necessary quantities which lead to the χ_P values.[35] Another difficulty in assessing the low-density jellium χ_P by using the observed values of the Rb or Cs susceptibility is the uncertainty in their band-structure effect.

These metals seem to have a considerable deviation from jellium: (i) The deviation of m_B^*/m from unity may (or may not) be an indication of the strength of the crystalline effect. Unfortunately, m_B^* defined by the following relation is not accessible experimentally:

$$m_B^*/m = N(\epsilon_F)/N_F(\epsilon_F) . \tag{3}$$

Here $N(\epsilon_F)$ and $N_F(\epsilon_F)$ are the density of states at the Fermi surface for the real metal and the free-electron gas, respectively. An optically measured effective mass is not necessarily equal to m_B^*.[48–50] As stated previously, the specific heat or the cyclotron effective mass is dressed with an unknown amount of the electron-electron and the electron-phonon interaction.[51] The diversity of the calculated values for m_B^* is so large that almost any experimentally observed χ_P value can be used to justify any given jellium χ_P by selecting a suitable m_B^* value. (ii) Even if one knows of the correct values of m_B^*, and if one can assume that m_B^* represents the band-structure effect on χ_P,

there was no logical method to integrate the band-structure effect into the Fermi-liquid theory. A new general theory recently developed by Vosko and Perdew[52] seems to be the most promising answer to these questions and will be discussed later.

The spin-lattice relaxation time T_1 of NMR gives some information on the electron-electron interaction.[53] The experimental results by Narath and Weaver[53] for K, Rb, and Cs suggest that the enhancement in χ_P for these metals is approximately the same. They concluded, however, that since the analysis of the T_1 data requires an additional assumption, their interpretation is of a tentative nature. They realized that further speculation must wait for the appearance of additional information on the χ_P value.

Wolff[54] pointed out that the ratio of T_1 in a high magnetic field and in a low magnetic field could be used as an indication of the electron correlation. Subsequent experimental and theoretical studies[55,56] revealed that the experimental ratio cannot be uniquely correlated to the amount of the electron-electron interaction without using assumed models.

The Knight-shift experiments for alkali-metal alloys by Kaeck[57] suggested that χ_P/χ_F is almost constant for all the alkali metals except Li. The data analysis was, however, based on certain assumptions which are reassessed recently by van Hemmen et al.[58,59] and by another group.[60]

A study of the pressure dependence of the Na (or K) susceptibility has unique advantages. It is believed that m_B^*/m is almost exactly one.[6,10,49,61-71] According to Ham,[49] dm_B^*/dr_S is very small for Na.[72] Besides, r_S of Na (~4) is about at the midpoint of the entire metallic range ($2 \lesssim r_S \lesssim 6$). The observed values of χ_P/χ_F and $d(\chi_P/\chi_F)/dr_S$ in conjunction with the RPA result for $r_S \ll 1$ were thought to give a reliable general trend of the many-body enhancement for the total metallic range. The influence of the remaining band-structure effect and particularly its r_S dependence has to be treated carefully, however, in order to reach the final solution of this problem.[52]

From two aspects of basic solid-state physics, the critical evaluation of the calculations for the wave functions in the simple metals and the experimental answer to the XC problem in the metallic range, the observation of the volume dependence of χ_P has been awaited a long time.[9,14,53,73] Now, for the first time, we have the answer in Li and Na.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Since the original work by Schumacher and Slichter[74] on the absolute measurement of χ_P in Li and Na, Schumacher's group and his associates have improved the accuracy and revised the results.[33,75-77] The initial value for Na is[74] (0.95 ± 0.1)×10^{-6} cgs volume units at 300 and 79 °K, and the revised value[76] is 1.12 ± 0.05 at 77 °K. The experimental error for Li is smaller, since the width of the conduction-electron spin resonance (CESR) line is narrower. The original value by Schumacher-Slichter[74] is (2.08 ± 0.1)×10^{-6}, and more recent values are[77] 2.09×10^{-6} at 298 °K and 2.18×10^{-6} at 4.2 °K with an accuracy of 5%.

The area under the CESR absorption curve is proportional to χ_P. Since it is difficult to measure the absolute magnitude of the resonance absorption, they first measured the CESR at a low field (a few gauss) and then measured the NMR signal in the same sample at a high field (a few thousand gauss) without changing the condition of a spectrometer system. The area ratio of the two resonance curves gives the χ_P value in units of the nuclear susceptibility which is well known.

The volume-dependence experiments measure the change in atomic susceptibility χ_P^A (or molar susceptibility), since the number of atoms does not change with the volume compression. The volume dependence of χ_F goes as $\Omega^{-1/3}$ and χ_F^A ($= \Omega \chi_F$) changes as $\Omega^{+2/3}$. In order to get a meaningful value for the change of χ_P^A or χ_P associated with a typical volume change, say 10%, due to hydrostatic pressure, the accuracy of the measurement has to be increased by one order of magnitude compared with the results by Schumacher's group.

It would have been a formidable task to increase the accuracy of the absolute value by this amount. They had to spend seven years to decrease the experimental error by a factor of 2. Fortunately what we needed was an improvement in the relative accuracy associated with the volume change.

The major source of systematic error in the initial value for Na was[33,75,78] the difficulty in estimating the area under the long tails of the CESR line, most of which are hidden in the noise. For the relative change due to pressure, however, as long as the shape and the width of the observed line are unchanged with pressure, the error from this source is of a minor importance.

Background spurious signals are another problem which could contribute to the systematic error. These signals have two sources: (i) a direct electromagnetic pickup and (ii) weak but broad near-zero-field EPR lines caused by some impurities. The swing of the magnetic field sweep for the present Na CESR measurement was over 100 G. Some amount of direct pickup is almost inevitable, and this contributes to the spurious background signal. A triangular shaped field sweep was used. The CESR signals were measured both during the upward and the downward sweeps. The background signals had opposite polarity for these

successive sweeps and tended to cancel one another during an area integration process. The contribution of the pickup signals was unchanged with pressure. We confirmed that the observed pressure dependence of χ_P did not change when the sweep amplitude, and thereby the amount of pickup, was changed.

The impurity EPR signals were most troublesome. Their intensity changes with temperature and often with pressure. This problem and its solution will be described later.

The effect of random statistical noise was reduced by automating the measurement procedures and taking the statistical average of many hundreds of measurements.

The block diagram of the experimental setup is shown in Fig. 1. The CESR and the NMR signal of the sample, which is enclosed in a BeCu high-pressure bomb, are detected with a Pound-Knight type spectrometer. Since the magnetic field is not modulated, contrary to conventional practice for a magnetic-resonance experiment in solids, the spectrometer response at low frequency had to be improved by increasing the time constant of the automatic level control of the spectrometer.

The rf frequency of the spectrometer was 10.5 MHz for Na. For Li 10.5 and 14.9 MHz were used. It was important to use spurious-EPR-free material for the rf coil and its support. A clean enamel-insulated copper coil with a thin coat of epoxy resin (Hardman, Inc., Belleville, N. J., Extra Fast Setting) was satisfactory at room temperature. A similar coil covered with thin Mylar films covered in turn with the epoxy coating worked better at 200 °K.

The dispersed Na metal was purchased from Matheson, Coleman, and Bell. The Na particles have a nominal size of 1 μm and were dispersed in a light oil when received. The light oil was replaced by high-pressure transmitting oil which has been precleaned. Since the skin depth at room

temperature is ~30 μm, the penetration of rf is complete and no dispersion-mode signal was observed. The CESR T_1 for this sample was 3 $\times 10^{-6}$/T. The room-temperature linewidth of the derivative curve was 11 Oe peak to peak. We also made dispersion samples with an ultrasonic technique, but we did not use these homemade samples for the final data taking, since their CESR width was somewhat larger than that of the purchased samples.

The Li dispersion was prepared with a high-speed mechanical agitator. The original material was purchased from Matheson, Coleman, and Bell, the nominal purity being 99.9%. The T_1 value for the Li sample ranged between 4 and 9 $\times 10^{-8}$ sec at room temperature. We prepared a finer (5–30-μm particle diam.) and a coarser (20–80 μm) dispersion. The latter sample showed a slight mixture of the dispersion-mode signal. The observed pressure dependence, $\chi_P^A(P)/\chi_P^A(0)$ was the same as for the finer sample.

The density of the dispersed sample was increased by spinning the sample ampoule in a centrifuge. The increase of the density of metallic particles enhanced the signal intensity of the CESR and the NMR without increasing the background signals. If the dispersion was too tightly packed, however, a *hysteresis* effect was noticed. The measured value of χ_P^A did not return to a zero-pressure value after the pressure was released, the difference being a few percent. The anomaly was found to take place after an initial pressure (~2000 kg/cm^2) was applied. Beyond this pressure range the pressure dependence of χ_P^A was completely reproducible during the increase or decrease of pressure. The slope $d\chi_P^A/dP$ in the higher-pressure range was the same as that for the *nonhysteresis* samples. The hysteresis effect was probably due to contacts between the particles caused by the pressure. It was noticed that coating with a small amount of oleic acid reduced this effect. The coarse-particle samples tended to have more hysteresis problems.

The elimination (or at least the minimization) of the impurity background signals was the most difficult problem in this experiment. These signals did not usually originate from the sample dispersion itself. Their amplitude was not large; they were often not noticeable on the monitor oscilloscope screen. Signal accumulation in a signal averager, however, revealed very broad background signals (over 1000-G wide). Since the intensity of these signals was distributed over a large magnetic field range, their integrated intensity was appreciable compared with the area of the real signal. These signals were believed to be due to the EPR signals of the impurities from various origins. At near-zero field, the rf power
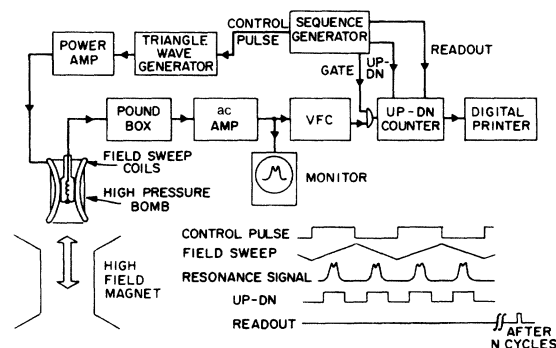

FIG. 1. Block diagram of the CESR and the NMR area-measurement apparatus. The timing diagrams are also shown.

absorption had a peak rather than a dip, which would be expected if the cause was the magneto-resistance.

The intensity and the width of the signal changed with temperature. The integrated area of these signals often depended on the pressure as well. Our preliminary data[79] for Na contained appreciable error due to this origin. A clean inside surface of the sample container was essential. Proper shielding of the rf coil was necessary for the inside wall of the BeCu bomb which generated a strong spurious signal at 200 °K.

After carefully cleaning the coil and sample ampoule the pressure dependence of the residual background signals was checked. Their contribution to the observed pressure dependence of χ_P^A was negligible. When the amplitude of the field sweep was changed, the ratio between the area of the spurious signal and the real signal would have changed. Our pressure-dependence data were un-affected by the change in the sweep amplitude. Since the intensity of the background signals depends strongly on temperature, their pressure dependence would most likely depend on the temperature. Our final results gave the same pressure-dependence values for room temperature and for 200 °K. We concluded that the present pressure data is not affected by the residual-impurity effect.

The precautions for the NMR calibration of the CESR signal are as follows: (a) Any saturation of the NMR line would make it unsuitable for use as a calibrator for the CESR line, since the degree of saturation might change with pressure. Therefore, any saturation effect must be eliminated.[77] (b) Motionally narrowed NMR lines at room temperature have their width determined by the inhomogeneity of the magnet. By changing the amount of the inhomogeneity of the magnet we confirmed that our results were independent of the field homogeneity. Since an increase of the field sweep amplitude did not change our results, the total intensity of the NMR line was indeed covered by the present field swing. Although the line did not change with pressure at room temperature, the lifting of the motional narrowing took place at approximately 4000 kg/cm² at 200 °K. The pressure-dependence data for χ_P^A showed no change at this pressure. We believe that the change of the line shape of the NMR signal due to these origins does not affect the present results. (c) If the sweep speed is too fast, an adiabatic condition is violated and the NMR line is distorted. The degree of distortion ("wiggle") could depend on the pressure. Since it was difficult to avoid this type of distortion completely for the motionally narrowed NMR line, the possible effects on the pressure data were checked experimentally. The speed of

the sweep was changed by a factor of 6. The results were independent of the sweep speed. As a second check, the atmospheric pressure value of χ_P^A was measured at 77 °K, where the motional narrowing is absent and no wiggle exists. We obtained the same value as that at room temperature. The same check was made on the CESR lines. We concluded that any small distortions of the resonance lines due to the transient effect do not affect our results.

As mentioned before, the most difficult correction for the absolute measurement of χ_P, the tail-area estimate of the Lorentzian-shaped CESR line[33,75,76] fortunately is not a serious problem in the present experiment. In order to check the importance of the effect of the tail cutoff in our pressure change, $\chi_P^A(P)/\chi_P^A(0)$, we reduced the sweep amplitude by a factor of 3. Although the observed (apparent) value of $\chi_P^A(0)$ decreased appreciably due to the increase of the uncounted tail area, the ratio $\chi_P^A(P)/\chi_P^A(0)$ did not change. The linewidth was unchanged with pressure.

Since the nuclear susceptibility is inversely proportional to T, the temperature of the bomb was monitored with a thermocouple.

The field sweep coil was wound directly on the outside of the bomb. The swing of the sweep was ±125 Oe for the CESR observation. The sweep rate was 6 or 12 Hz. The triangular shape of the sweep at the sample cavity in the bomb was distorted due to the eddy-current effect. When the sweep direction was reversed, the inside field did not follow the reversal immediately. The essential part of the field sweep in the bomb was, however, sufficiently linear.

The NMR signal was observed in a Varian 12-in. magnet. The same sweep coil was used. The sweep amplitude was, however, reduced to $\frac{1}{20}$, since the NMR line is narrow at room temperature. The distortion at the peak of the wave form in the bomb was worse, because of the presence of the pole pieces of the magnet. The center parts of the sweep where the NMR line was displayed were sufficiently linear, however.

The high-pressure bomb, the sweep coil, and the spectrometer were rigidly suspended on a sliding deck. The deck was rolled into and out of the magnet. The deck was moved by a digitially controlled stepping motor. The location of the deck, whether inside or outside the magnet, was precisely reproducible.

The high pressure was generated with a Bridgman-type ram which was purchased from Harwood Engineering Co. and extensively modified to obtain satisfactory operation. In the room temperature measurement the pressure transmitting liquid was petroleum ether. A mixture of pentane and n-butyl butane (equal amounts by volume) was
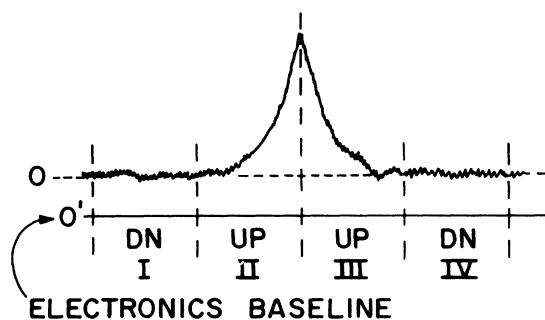
FIG. 2. Automatic area integration of the resonance curve. The digital integrator "counts up" during periods II and III, "counts down" during periods I and IV, and cancels the area between the base line of the resonance curve (0) and the electronics base line (0').

used for the 200 °K experiment. Both liquids were pretreated with sodium-metal pieces.

The integration of the resonance curves was performed as follows (Fig. 1): The output of the spectrometer was sent to a voltage-to-frequency converter (VFC). The frequency of the pulse output of the VFC was precisely proportional to the input voltage. The number of pulses was counted with an up-down counter. The combination of the VFC and the counter acts as a digital integrator, and the integration accuracy is determined by the accuracy of the VFC alone. Thus we could avoid the drift problem of an analog integrator. Besides, the counter mode can be changed electrically by sending an up-down command signal (UP-DN). In the up-count mode the content of the counter increases as the pulses enter the counter. In the down-count mode the counter content decreases. Another advantage of this digital integrator is that many integrated signals can be accumulated in the counter in a digital form and can be printed out on a read-out command.

A troublesome problem associated with an electronic integrator is the integration error due to an improperly set zero level at the input. The dc output level of the signal amplifier (O' in Fig. 2) has to be exactly adjusted to the base line of the signal (O in the figure). If O' is lower than O, as is the case shown in the figure, the integrator integrates the total area between the signal and the electronic base line O'. The integrator output keeps increasing even after the integration of the resonance curve is completed. If O' is higher than the O level, the integrator output keeps decreasing after the desired integration is completed. It is very difficult to adjust the O' level properly by monitoring the signal on a scope screen because of the random noise. Even if one can adjust the electronic base line perfectly once, the electronic base line tends to drift gradually and re-

quires continuous readjustments.

This problem was solved as follows: The integration period was divided into four equally spaced ranges (I, II, III, and IV in the figure). Ranges II and III contain the resonance line whose center was approximately adjusted to the boundary of II and III. Ranges I and IV correspond to the base line of the signal. The electronic base line O' was adjusted so that the signal (including the associated noise) level was always higher than O'. The counter was operated in the down mode at ranges I and IV and in the up mode at the center ranges II and III. The areas between the electronics and the signal base lines cancel. The counter content at the end of range IV is the area under the resonance curve alone. An input gate of the counter (Fig. 1) opens only during the integration periods, ranges I through IV. After the required number of signal accumulations, the counter content was printed out. The same procedures were repeated alternatively for the CESR and the NMR lines.

It is important to alternate the procedure as rapidly as possible in order to minimize the calibration error due to the gain drift of the electronic system between the CESR and the NMR measurements. It is not desirable, however, to move the bomb-spectrometer system too fast. The mechanical disturbance of the sample dispersion should be avoided. The compromise we adopted was as follows: (i) The NMR signals were accumulated 640 times. (ii) The CESR was also measured 640 times. (iii) Then the procedures (i) and (ii) were repeated 5 times. The field sweep rate was 6 or 12 Hz. The same sequence was repeated at each pressure point.

A sequence generator, which is often called a word generator, is a homemade universal programmer. The appropriate commands, such as triggering a triangle wave generator, gating the VFC output, and the up-down and the readout instructions for the counter, are issued at appropriate times. The programming can be changed by altering plug positions at a diode matrix board.

The values for $\chi_P^A(P)/\chi_P^A(0)$ observed under various conditions were compared. The effect of the size of the particles, the degree of their packing, and the sweep rate and amplitude did not affect the experimental results as stated previously. The influence of the amount of the sample in the rf coil was also checked. If the effective rf field in the coil was not uniform over the sample, a possible deformation of the coil accompanying the pressure change would have changed the inhomogeneity of the rf field. If the change in the inhomogeneity had any effect on the experimental values, the results would have been dependent on the amount of the sample. We checked the effect of the oleic
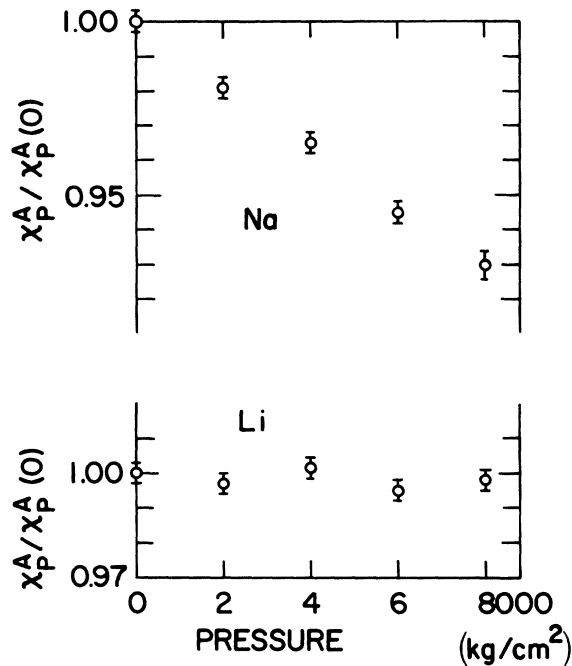
FIG. 3. Pressure dependence of atomic susceptibility χ_P^A for Na and Li. χ_P^A is normalized to its atmospheric value.

acid which kept the sample particle surface oxide free. We compared the results obtained using enamel-wire coils and clean bare copper coils which occasionally short circuited between turns as the pressure was increased. The results obtained using petroleum ether and the two-component mixture mentioned before were compared. The time constant and the rf level of the spectrometer were varied. It was confirmed that the results were independent of the changes in these experimental conditions.

For Na six sets of pressure data were taken under different conditions at room temperature, and three sets were obtained at 200 °K. No systematic differences were noticed among all the data. Since the CESR of Li has much better signal-to-noise ratio, two sets of data at room temperature were sufficient.

The experimental results are shown in Fig. 3. The room-temperature data are shown in the figure. The data at 200 °K for Na are the same as that at room temperature within experimental error ± 0.3%.

The measured pressure dependence of the susceptibility is converted into the volume dependence by using available compressibility data. Swenson's values[80] of the $P - T - V$ relation are used for Li. For the compressibility of Na, Beecroft and Swenson's values[81] are utilized with the subsequently published correction for their pressure calibration.[82] The volume dependence of χ_P^A (the circles)

and χ_P (the triangles) are shown in Fig. 4. Both the susceptibility and the volume are normalized to their atmospheric values.

A striking deviation from the free-electron slope, $d\ln\chi_F/d\ln V = -\frac{1}{3}$, is noticed for Li.

The absolute value of $\chi_P(0)$ was also obtained from the present data, although this was not the main objective of the present experiment. The uncertainty in the estimate of the hidden tails for the CESR lines, a possible effect of the residual background signal which does not affect the pressure results, and uncertainty in the calibration of the field sweep were the main sources of experimental error in the absolute values. The amount of the errors due to the three causes is believed to be approximately the same.

The results are:

$$[\chi_P(0)]_{Na} = (1.07 \pm 0.03) \times 10^{-6},$$

$$[\chi_P(0)]_{Li} = (1.98 \pm 0.04) \times 10^{-6}.$$

Previously obtained values by other workers using various methods are compared with our values in Table I. All the recently measured values agree with the present values, within the quoted experimental errors, except the χ_P deduced from the dHvA effect, where the ambiguity and the uncer-
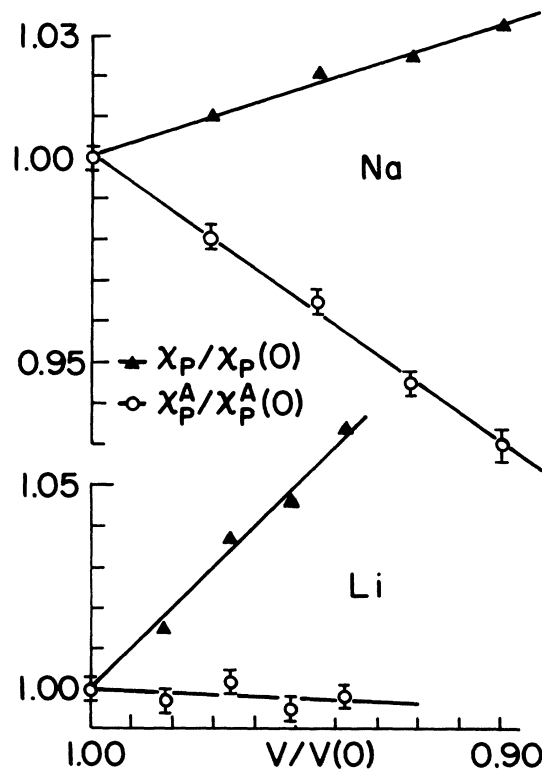

FIG. 4. Volume dependence of the atomic susceptibility χ_P^A and the volume susceptibility χ_P. The susceptibility and the volume are normalized to their atmospheric values, respectively.

TABLE I. Summary of the observed values for χ_P in Li and Na.

Li	Na		
$(10^{-6}$ cgs volume units)			
2.08 ± 0.1	0.95 ± 0.1		Schumacher and Slichter, CESR area.[a]
	0.89 ± 0.04	$4.20\,°K$	Schumacher and Vehse, CESR area.[b]
	1.13 ± 0.05	$20\,°K$	
	1.12 ± 0.05	$77\,°K$	Schumacher and Vehse, CESR area.[c]
	1.09 ± 0.08	$4.2\,°K$	
2.09 ± 0.06		room temp.	Kettler, Shanholtzer, and Vehse, CESR area.[d]
$2.09 \pm 5\%$		room temp.	Kettler, Shanholtzer, and Vehse,
$2.18 \pm 5\%$		$4.2\,°K$	CESR area.[d]
1.96 ± 0.10		$300\,°K$	Hecht, CESR saturation; no temp. dependence was noticed at 300, 77, and $1.5\,°K$.[e]
2.13 ± 0.07	1.09 ± 0.05		Ryter, day-shift.[f]
	1.04 ± 0.04	$\sim 4.2\,°K$	Dunifer, Pinkel, and Schultz, spin waves.[g]
	$1.77,\ 1.55$	$< 4.2\,°K$	Knecht, Randles, and Shoenberg, dHvA effect.[b]
	$1.77,\ 1.4$	$< 4.2\,°K$	Knecht, Randles, and Shoenberg, dHvA effect.[i]
1.98 ± 0.04		room temp.	Present data, CESR area.
	1.07 ± 0.03	room temp. and $200\,°K$	Present data, CESR area

[a]Schumacher and Slichter, Ref. 74. Although these values have been quoted by many authors, these results are in error. See Ref. 33.

[b]Reference 75 (1960). The same notion as in Ref. a may be applicable to this value.

[c]Reference 33.

[d]Reference 77.

[e]Reference 83.

[f]Reference 84, derived from ξ given in Ref. 84 and the Knight shift.

[g]Reference 17, derived from B_0 in their paper ($B_0 = -0.215 \pm 0.03$) and the observed cyclotron resonance mass ($m^*_{CR}/m = 1.24 \pm 0.02$, Ref. 85) by using the relation $\chi_P/\chi_F = (m^*_{CR}/m)(1 + B_0)^{-1}$. The free-electron susceptibility χ_F ($= 2.589\ r_s^{-1} \times 10^{-6}$) is determined by the r_s value corresponding to the lattice constant at $5\,°K$ (Ref. 86). The effect of the difference in r_s values for a bcc structure ($r_{s\,bcc} = 3.931$) and for an hcp structure ($r_{s\,hcp} = 3.935$) is much smaller than the experimental uncertainty in m^*_{CR} and in B_0.

[h]From B_0 derived from dHvA effect (Ref. 35) as quoted by Dunifer $et\ al.$ in Ref. 17.

[i]Reference 35. Presumably due to the martensitic transformation in Na, the B_0 values obtained from the dHvA effect contain a relatively large uncertainty. The inherent ambiguity of this method of obtaining B_0 is discussed in Ref. 35. See also Ref. 87.

tainty in deriving χ_P/χ_F are large. In particular, the present values agree well with the one derived from the spin-wave experiment by Dunifer, Pinkel, and Schultz.[17]

III. COMPARISON WITH THEORETICAL PREDICTIONS—A. THE VOLUME DEPENDENCE OF P_F

It is not obvious that the effect of exchange and correlation almost cancel each other[88] in the band-structure and the wave-function calculations. The distortion of the Fermi surface could be affected significantly by the nonlocal exchange and correlation.[89] It is, however, generally believed that the P_F value is insensitive to the electron-electron interaction.[90]

The theoretical predictions for P_F, which are usually based on the one-electron approximation, are compared with the experimental values derived
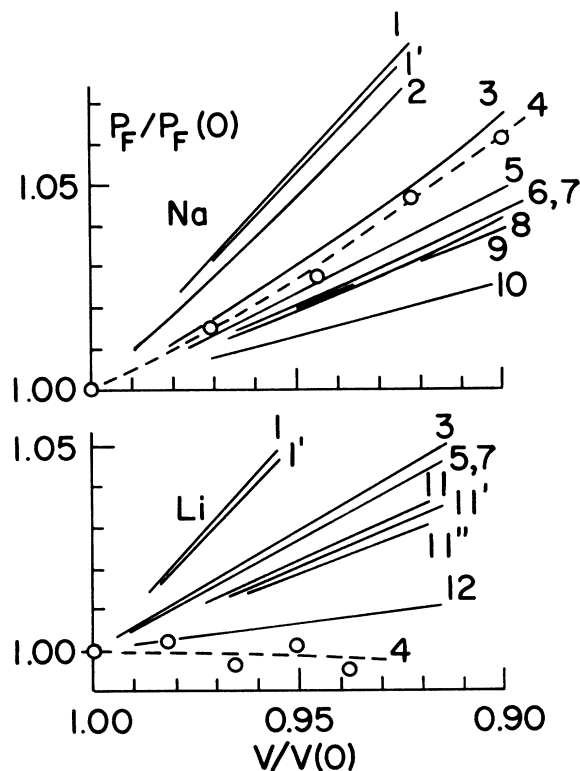
FIG. 5. Volume dependence of P_F for Na and Li. Both P_F and V are normalized to their atmospheric values, respectively. 1, Holland, Ref. 91; 1', Heighway and Seymour, Ref. 92; 2, Alekeev and Kochkin, Ref. 93; 3, Asano and Yamashita, Ref. 9; 4, present experimental values; 5, Micah, Stocks and Young, Ref. 63; 6, Brooks, quoted by Renedek and Kushida, Ref. 14; 7, Moore and Vosko, Ref. 90; 8, Tong and Pant, Ref. 5; 9, Ritter and Gardner, Ref. 12; 10, Kjeldaas and Kohn, Ref. 97; 11, Perdew, Nickerson, Vosko, and Moore, spherical cell model, Ref. 72; 11' Perdew, Nickerson, Vosko, and Moore, APW, Ref. 72; 11'' Perdew, Nickerson, Vosko, and Moore, all OPW's, Ref. 72; 12, Mahanti, Ref. 99.

from the observed K and χ_P using Eq. (1). The volume dependence of P_F was obtained by combining the present values for $\chi_P(V)$ with the previous pressure measurement of K.[14] The results are indicated in Fig. 5 by the circles for Li and Na. The theoretical predictions are also shown in the figure. The P_F value and the volume are normalized to their respective values at atmospheric pressure.

As stated previously,[8-12] it is our belief that the basic understanding of metal physics is incomplete until the numerically correct wave functions can be derived for the simple metals with an accuracy of, say 10%. This would have to take into account the usually neglected effect of the electron-electron interaction and other approximations. The eigenvalues ϵ_i, are not a crucial test of the basic equa-

tion (2).

For Na all the theories (1-10 in Fig. 5, except 4 which is the experimental curve) are correct in their general trend. The charge density at the nucleus increases as the atomic volume is squeezed. This is in agreement with a naive picture.

A simplified pseudopotential approach was proposed by Holland[91] and extended by Heighway et al.[92] to include the second-order correction. Their results are shown by 1 and 1', respectively. The first-order result by Holland is

$$P_F = |\gamma|^2 / \Omega \beta , \qquad (4)$$

where

$$\gamma = 1 - \sum_n b_n \alpha_n , \qquad (5)$$

and

$$\beta = 1 - \frac{1}{\Omega} \sum_n b_n b_n^* . \qquad (6)$$

α_n is the amplitude of the nth core function at the nucleus $\Psi_n(0)$, and

$$b_n = \int \Psi_n^*(\vec{r}) d\vec{r} . \qquad (7)$$

The volume dependence of P_F in first order is simply

$$d\ln P_F / d\ln V = -1/\beta , \qquad (8)$$

if one neglects the volume dependence of α_n. The P_F value derived from Eq. (4) in conjunction with the experimental χ_P value[91] gives a Knight shift which is 20% larger than the observed value. This is remarkably good agreement if one considers the simplicity of this model. The volume dependence given by Eq. (8) is, however, twice as large as the observed value. The second-order correction hardly improves the volume dependence.[92] This example may indicate the usefulness of the volume-dependence experiment in revealing the adequacy of the various models.

Alekseef and Kochkin[93] calculated the volume dependence of P_F for Na (curve 2) using the Wigner-Seitz cellular method. They neglected the XC effect assuming a parabolic band structure. K is about a factor 4 too large. The predicted volume dependence of P_F is 60% larger than the experimental value.

The augmented-plane-wave (APW) calculation by Asano and Yamashita[9] (curve 3) agrees well with our experimental data in spite of their claimed uncertainty in deriving the numerically correct value of P_F (and its volume dependence) based on the present knowledge of the crystal potential. The calculated values critically depend on the choice of the crystal potential. It may be said that the present experiment is a critical test for the

crystal potential. Asano and Yamashita gave the P_F values also; $P_F = 0.40$ with the Hartree-Fock approximation and 0.54 with an $X\alpha$ method ($\alpha = 0.8$). The experimental value is 0.445 ± 0.022.[8]

Micah, Stocks, and Young[63] calculated $P_F(V)$ using a "generalized orthogonalized-plane-wave (OPW) method."[94] They obtained an almost perfect agreement (~1%) for P_F in Na (Table 5 in Ref. 94). The volume dependence of P_F (curve 5) is in reasonable agreement with the experimental value.

Curves 6 and 7 are indistinguishable in Fig. 5. One is derived by Brooks[95] using a quantum defect method; the other is the calculation by Moore and Vosko[90] based on a modified cellular approximation with a Prokofjev potential. Moore and Vosko's value for P_F, which is expressed in terms of the ratio between P_F and its atomic value P_A, agrees with the experimental value within 10%. Curve 8 was calculated by Tong and Pant[5] with a Kohn-Sham self-consistent scheme. Their P_F for Na is in good agreement with the observed value. More recently Ritter and Gardner[12] calculated $P_F(V)$ using the pseudopotential method. The results are shown in curve 9. Their P_F agrees with the observed value within 3%. Although they are more optimistic about their volume-dependence calculation, their P_F value for $V/V_0 = 0.90$ is approximately 40% smaller than the measured value.[96] Curve 10 is a relatively old variational calculation by Kjeldaas and Kohn is 1956.[97]

Although the P_F values, experimental and theoretical, increase with decreasing volume, the experimental results indicate that the increment is considerably smaller than is expected from a straight normalization effect of the wave function which predicts P_F going as V^{-1}. But the observed fact that P_F does increase with a volume decrease is in contrast to the assumption of volume independent P_F. This assumption has been used in interpreting the NMR alloy data.[98]

The Li results are also shown in Fig. 5. The experimental results (curve 4) indicate that P_F is unchanged or even tends to decrease with decreasing volume, whereas all the theories predict that P_F increases much the same way as in the case of Na. The slopes given by Holland et al. (1 and 1') are about the same as for Na. Their volume dependence is roughly what is to be expected from a straight normalization effect of the wave functions. The good agreement obtained by Asano and Yamashita, by Micah, Stocks, and Young, and by Moore and Vosko for Na is absent for Li. Perdew, Nickerson, Vosko, and Moore[72] calculated the volume dependence of P_F using three independent methods: the spherical cell, the APW, and the OPW-pseudopotential method. They

calculated the direct contribution P_F^d, excluding the core-polarization effect P_F^{cp}.[10,13] Curves 11 and 11' are their results based on the cellular and the APW method, respectively. Their OPW calculations using over 100 OPW's are indicated by 11''. Since the results obtained using these three independent methods are in good agreement, they believe that the calculations of P_F^d are reliable. However, P_F^d by itself does not agree with the present volume-dependence experiment.

Mahanti[99] estimated the effect of the core polarization on the volume dependence of the total $P_F(= P_F^d + P_F^{cp})$. Based on the previously calculated values of P_F^d and P_F^{cp}, he demonstrated the possibility that the total P_F could have a considerably smaller volume dependence than P_F^d. His result is shown by the curve 12. Although a reasonable agreement with the experimental results is achieved, it seems that more detailed calculations are required to substantiate this estimate.

We feel that the first-principles calculation of the electronic structure of the simplest metal Li is still a challenge for the solid-state theoreticians.[100]

To conclude this section, the present experimental results for Na are in agreement with all the theories within ~±100%. Some of the theories agree within 10%, which is quite satisfactory in view of the approximations involved. The Li results do not agree with any of the first-principles calculations. The correlation effect may not be important.[90] The relativistic effect is negligible for Li.[90] The core polarization has to be taken into account.[99] Finally it is noted that some doubt has been cast on the validity of the working equation (1) for Li. Since the anisotropy in $|\chi_{k_F}(0)|^2$ and ϵ_k is large,[72] is it valid to express K as a product of the two averaged values, $\langle|\chi_{k_F}(0)|^2\rangle$ and χ_P? How important is the quasiparticle anisotropy effect[101] in the Knight shift for Li?

IV. COMPARISON WITH THEORETICAL PREDICTIONS—B. THE VOLUME DEPENDENCE OF χ_P

The main purpose of the comparison between the observed susceptibility and the theoretical predictions is to get a clear picture of the degree of XC enhancement of the susceptibility. The ratio χ_P/χ_F, rather than χ_P itself, is more appropriate for this purpose since χ_P/χ_F emphasizes the enhancement.

Table II summarizes the experimentally derived values for χ_P/χ_F and $d(\chi_P/\chi_F)/dr_S$ together with the most recent theoretical results which will be discussed later.

As stated in the Introduction it is most tempting to plot χ_P/χ_F vs r_S by smoothly connecting the RPA slope for $r_S \ll 1$, the χ_P/χ_F value and its slope for Na, and to compare the result with numerous theoretical predictions based on the jellium model,

TABLE II. The enhancement in the susceptibility χ_P/χ_F and its derivative $d(\chi_P/\chi_F)/dr_S$.

	Li	Na
r_S	3.26	3.99
$(\chi_P/\chi_F)_{exp}$ [a]	2.50 ± 0.05	1.65 ± 0.05
$(\chi_P/\chi_F)_{theory}$ [b]	2.68	1.62
$[d(\chi_P/\chi_F)/dr_S]_{exp}$ [a]	−1.44 ± 0.12	0.04 ± 0.03
$[d(\chi_P/\chi_F)/dr_S]_{theory}$ [b]	−1.137	0.011

[a] χ_F is derived from the relation; $\chi_F = 2.589\ r_S^{-1} \times 10^{-6}$.
[b] Reference 134.

since Na is believed to be the best replica of the ideal jellium. Some of the results were shown in Ref. 1. As stated before, however, this attempt could not escape from a pitfall due to the lack of knowledge about the remaining band-structure effect.

Postponing a detailed discussion of the crystal-

line effects, let us summarize the theoreticians's predictions for the χ_P/χ_F vs r_S relations in Fig. 6. These are all for jellium models. No crystal-line effects (band-structure effects) are accounted for. Since it is not our purpose to discuss the theoretical aspects of the many-body effects, we restrict ourselves to brief comments on these curves.

The curves, P (Pines), SI (Silverstein), and SH (Shimizu) were calculated based on a Sampson-Seitz scheme[46] with improved expressions for the correlation energy. It is noted that the inclusion of the correlation effect supresses the exchange enhancement at large r_S; without the correlation suppression χ_P/χ_F becomes infinite at $r_S \sim 6$ as mentioned before.[32] The correlation suppression seems, however, to be overestimated in these models.

The theories by Singwi's group (LST, VS, BPS, SSTL) were derived from a "self-consistent re-
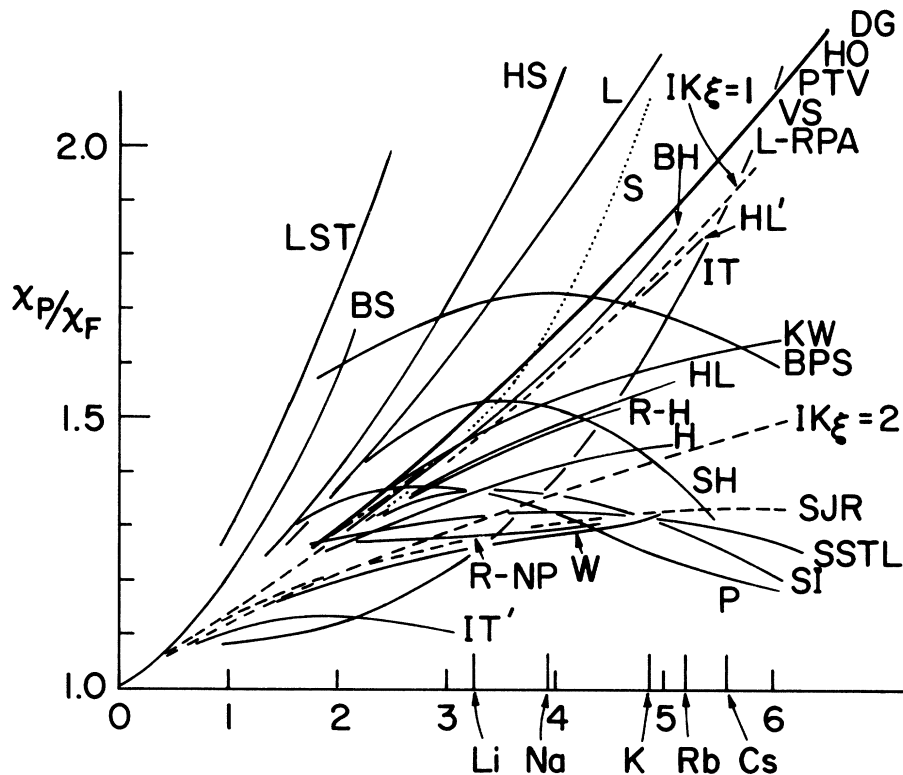

FIG. 6. Theoretical predictions for many-body susceptibility enhancement χ_P/χ_F as a function of Wigner-Seitz radius r_S. No band-structure effects are accounted for (a jellium model). LST, Lobo, Singwi, and Tosi Ref. 102; BS, Brueckner and Sawada, Ref. 29, see also Ref. 30; W, Watabe, Ref. 103; HS, Hasegawa and Shimizu, Ref. 104; DG, Dupree and Geldart, Ref. 105; HO, Hamann and Overhauser, Ref. 106; PTV, Pizzimenti, Tosi, and Villari, Ref. 23, VS, Vashishta and Singwi, Ref. 107; IT, Isihara and Tsai, Ref. 108; BPS, Bhattacharyya, Pathak, and Singwi, Ref. 109. HL, Hedin and Lundqvist, Ref. 18; R-H, Rice based on a Hubbard model, Ref. 110; R−NP, Rice, based on a Nozières-Pines's model, Ref. 110; H, Hedin, quoted in Rice's article, Ref. 22; SH, Shimizu, Ref. 111; SSTL, Singwi, Sjölander, Tosi, and Land, Ref. 112; SI, Silverstein, Ref. 113; P, Pines, Ref. 114; KW, Keiser and Wu, Ref. 115; L, Lam, Ref. 116; L-RPA, Lam, RPA, Ref. 116; SJR, Shastry, Jha, and Rajagopal, Ref. 117; BH, von Barth and Hedin, Ref. 118; S, Singh, Ref. 119; HL', Hedin and Lundqvist, Ref. 120; IT', Isihara and Tsai, Ref. 121; $IK_{\xi=1}$, Isihara and Kojima, Ref. 122; $IK_{\xi=2}$, Isihara and Kojima, Ref. 122.

sponse function scheme." In their results,

$$\frac{\chi_P(\vec{q}\omega)}{\chi_F(\vec{q}\omega)} = \frac{1}{1 - I(\vec{q})\chi_F(\vec{q}\omega)} \ . \tag{9}$$

The molecular-field parameter $I(\vec{q})$,[123] which represents an additional magnetic field felt by an electron surrounded by other magnetically polarized electrons, is written in terms of pair correlation functions [or their Fourier transform structure factor $S(\vec{q})$].[102,107,109,112] $\chi_P(\vec{q}\omega)$ and $S(\vec{q})$ are bootstrapped in such a way as to satisfy a *necessary* condition, the fluctuation-dissipation relation.[124] The curve BPS (Bhattacharyya, Pathak, and Singwi) is a scaled-up version of the curve SSTL (Singwi, Sjölander, Tosi, and Land) in order to fit the experimental value of χ_P/χ_F for Na.

Isihara's theories (IT; IT′; IK, $\xi = 1$; IK, $\xi = 2$) are based on statistical mechanical calculations, applicable to a relatively high-density region, $r_s \lesssim 3$.[125] ξ is a cut-off parameter for the q integration.

The curves DG (Dupree and Geldart), HO (Hamann and Overhauser), PTV (Pizzimenti, Tosi, and Villari), VS (Vashishta and Singwi), and L-RPA (Lam) agree with each other almost completely, in spite of differences in their models and their methods of calculation. These curves are also close to BH (von Barth and Hedin) and IK, $\xi = 1$. The agreement of these theories is often quoted as a strong indication that these results are indeed a correct answer to the susceptibility enhancement in jellium.[23,105,118,119] This statement seems to be quite plausible: A relatively orthodox Green's function approach (DG), the PTV theory based on the framework of Landau theory combined with the correlation treatment by SSTL, a different renormalization approach by HO, BH and HL′ theory based on the density-functional formalism by Hohenberg, Kohn, and Sham,[126,127] and an ingenious self-consistent method by VS in lieu of a frontal attack by means of many-body methods[128] all agree with each other. Even a relatively simplified theory, S (Singh), agrees with these results for $r_s < 4$. Although L-RPA and IK, $\xi = 1$ are in agreement with these calculations, the authors seem to prefer L and IK, $\xi = 2$, respectively.

Despite the agreement among the theories, it is highly desirable that the results should be compared with experiments. Unfortunately, an important bridge between the jellium model and real metals was missing until recently.

All the conduction electrons in the real metals are subjected to the periodic crystalline potential in addition to the mutual interactions among the electrons. The most common practice to take into account the crystalline effect is to use the effective mass m_B^*. Silverstein[113] proposed the following equation:

$$\chi_{\rm XCB} = \frac{\chi_{\rm XC}}{1 + (m/m_B^* - 1)\chi_{\rm XC}/\chi_F} \ , \tag{10}$$

where $\chi_{\rm XC}$ and $\chi_{\rm XCB}$ are the spin susceptibilities which include the XC effect alone (the jellium susceptibility) and the real-metal susceptibility with both the XC and the crystalline effect, respectively. Equation (10) is based on the assumption that the crystalline effect affects the susceptibility via a modification of the kinetic energy alone. The XC effect is assumed to be unchanged. The validity of these assumptions is not clear, however.

The same equation can be derived (Appendix) using the Landau model by assuming that a Landau parameter,[129] $f_0^{s(a)}$, is not affected by the crystalline field. Both the band-structure effective mass m_B^* and the electron-electron renormalization effective mass $m_{\rm XC}^*$ are accounted for. This model gives the same relation as one of the proposed forms by Rice.[110]

$$\frac{1}{m_{\rm XCB}^*} = \frac{1}{m_{\rm XC}^*} + \frac{1}{m_B^*} - \frac{1}{m} \ . \tag{11}$$

More integral approaches have been proposed.[25,66,67] For instance, the results by Timbie and White[67] as quoted by Mahanti and Das[10] were rather surprising. The crystalline effect on the susceptibility enhancement χ_B/χ_F is less than 1% for all the alkali metals except Li, whereas the m_B^*/m values given by Ham[49] are 1.00, 1.09, 1.21, and 1.30 for Na, K, Rb, and Cs, respectively. They considered that for the susceptibility the changes in the wave functions and in the chemical potential reduce the influence of the crystalline effect represented by m_B^*. Using a naive molecular field model it appears that the increase in the density of states enhances $\chi_{\rm XC}$ in two ways: (i) $\chi_F(00)$ in Eq. (9) is enhanced by m_B^*/m, and (ii) the enchancement due to the molecular field, $[1 - I(0)\chi_F(00)]^{-1}$, is also increased via the enhancement in $\chi_F(00)$, *provided* the molecular field parameter $I(0)$ is not reduced by the crystalline effect.

A model Hamiltonian scheme proposed by Hedin[130] is another attempt to include the band-structure effect in the susceptibility, with some improvement:

$$\chi_{\rm XCB}(r_s)/\chi_F(r_s) = m_B^*\chi_{\rm XC}(r_s^*)/m\chi_F(r_s^*). \tag{12}$$

An effective interelectronic distance r_s^* is defined by

$$r_s^* = m_B^* r_s/m\epsilon \ , \tag{13}$$

where ϵ is the dielectric constant due to the core electrons. A similar concept of the effective r_s, but without ϵ, has been introduced[131] to account for

the susceptibility of semimetals.

It is quite clear that, unless this missing theoretical link is established, the present experimental slope $d(\chi_P/\chi_F)/dr_S$ for Na cannot be used to prove or disprove the particular jellium calculations. Other experimental data are more unreliable for this purpose. For instance, the χ_P/χ_F values derived from the spin-wave experiments[17] are 1.58 ± 0.07 for Na and 1.69 ± 0.06 for K. Within experimental error $d(\chi_P/\chi_F)/dr_S$ can be anywhere between the slopes predicted by S and by BPS, if one can assume the crystalline

effect is the same for both metals. The uncertainties are more serious for Rb and Cs.

For instance, if one selects rather arbitrarily Silverstein's relation (10) and the effective-mass slope given by Ham, [49] $d\ln m_B^*/dr_S = -0.159$ for Na; the slope of the jellium enhancement $d(\chi_{XC}/\chi_F)/dr_S$ can be derived from the experimental slope 0.04 ± 0.03 (Table II) as

$$d(\chi_{XC}/\chi_F)/dr_S = 0.15 \pm 0.03 , \qquad (14)$$

since

$$\frac{d(\chi_{XC}/\chi_F)}{dr_S} = \frac{d(\chi_{XCB}/\chi_F)/dr_S - (\chi_{XCB}/\chi_F)^2(m/m_B^*)(1/r_S)(d\ln m_B^*/d\ln r_S)}{[1 - (m/m_B^* - 1)(\chi_{XCB}/\chi_F)]^2} , \qquad (15)$$

from Eq. (10).

χ_{XC}/χ_F and χ_{XCB}/χ_F should be identified as χ_P/χ_F in Fig. 6 and $(\chi_P/\chi_F)_{exp}$, respectively. This value, Eq. (14), is close to the slope at $r_S \simeq 4$ for the consensus theoretical curves:

$$d(\chi_P/\chi_F)/dr_S = \begin{cases} 0.20 \text{ for DG, etc.} \\ 0.18 \text{ for BH, HL .} \end{cases}$$

The experimental deduction, however, does not necessarily support the consensus trend, because of the ambiguity in $d\ln m_B^*/d\ln r_S$ and the treatment of the crystalline effect in general.

The difficulty in the crystalline-effect correction is most dramatically observed in the case of Li, where this effect is very large. For example, let us adopt Eq. (10) again and Ham's values for the effective mass and its slope:

$$m_B^*/m = 1.65 \text{ and } d\ln m_B^*/d\ln r_S = -1.722 ,$$

or

$$m_{Bs}^*/m = 1.32 \text{ and } d\ln m_{Bs}^*/d\ln r_S$$

$$= -0.666 \text{ for } r_S = 3.26 .$$

Here m_{Bs}^* is the value calculated with a spherical approximation. The results are $d(\chi_{XC}/\chi_F)/dr_S = +0.14 \pm 0.04$, or $d(\chi_{XC}/\chi_F)/dr_S = -0.18 \pm 0.05$. The latter value corresponds to the spherical approximation. Since the m_B^* value and the distortion of the Fermi surface given by Ham is believed to be overestimated, [132] the slope of χ_{XC}/χ_F deduced from this model is likely smaller than 0.14 and does not agree with the slope of the consensus curves, $\simeq +0.18$.

It is essential to develop an integrated, rather than a heuristic, theory to account for the crystalline effect on the spin susceptibility. If the theory gives a reasonable agreement for Li, we would

be quite confident for Na, where the crystalline effect is much smaller than that of Li. We may expect to get a definitive experimental check for the jellium susceptibility calculation using our χ_P/χ_F and its slope for Na. In this way, we obtain, for the first time, a reliable experimental check of many-body interactions in the lower part of the metallic density range.

After the pioneering work by Hohenberg, Kohn, and Sham[126,127] and by Pant and Tong[133] to apply the density-functional formalism to the susceptibility theory, [118,120] Vosko and Perdew (VP) have developed an improved variational expression for an inhomogeneous electron gas. Now a simultaneous treatment of the band and the XC effect in real metals is feasible. The VP results are summarized as follows:

$$\chi_{XCB}^{-1}[n] \leq \chi_B^{-1}[n] + \Omega \int d\vec{r}\, d\vec{r}'\, \gamma[\vec{r}; n]$$

$$\times G_{XC}[\vec{r}, \vec{r}'; n]\gamma[\vec{r}'; n] , \qquad (16)$$

where the susceptibility is a functional of electron number density $n(\vec{r})$. χ_B is the susceptibility of the noninteracting electron gas affected by the band-structure effect alone. A functional γ is defined by

$$\gamma[\vec{r}; n] \equiv \sum_i \delta(\mu - \epsilon_i)|\phi_i(\vec{r})|^2 \Big/ \sum_i \delta(\mu - \epsilon_i) . \qquad (17)$$

Here ϕ_i and ϵ_i are the ith wave function and the eigenvalue, respectively, for the self-consistent single-particle Schrödinger equation derived from the Kohn-Sham scheme. μ is the chemical potential. $G_{XC}[\vec{r}, \vec{r}'; n]$ is derived from $m(\vec{r})$ dependent part of the XC energy E_{XC},

$$G_{XC}[n, m] \equiv E_{XC}[n, m] - E_{XC}[n] , \qquad (18)$$

where $m(\vec{r})$ is the magnetic moment density de-

fined by

$$m(\vec{r}) = \mu_e[n_\dagger(\vec{r}) - n_\downarrow(\vec{r})] \ . \qquad (19)$$

μ_e is the electron Bohr magneton. $G_{\rm XC}[\vec{r}, \vec{r}'; n]$ is the leading term of the expansion for $G_{\rm XC}[n, m]$ with respect to m,

$$G_{\rm XC}[\vec{r}, \vec{r}'; n] = \delta^2 E_{\rm XC}[n, m]/\delta m(\vec{r})\delta m(\vec{r}')\big|_{m=0} \ . \qquad (20)$$

Equation (16) is a natural extension of the equation given by Kohn and Sham,[127]

$$\chi_{\rm XCB}[n] = \chi_B[n] + \Omega^{-1} \int d\vec{r}[\chi_{\rm XC}(n(\vec{r})) - \chi_F(n(\vec{r}))] \ . \qquad (21)$$

The result (16), when $\leq$ is replaced by $=$, reduces to the Sampson-Seitz-type approach,[45,46,113] when (i) the wave functions at the Fermi surface are of plane-wave form, and (ii) $n(\vec{r})$ is uniform. The susceptibility expression based on Landau's Fermi-liquid theory[40] gives the same *formal* results. The VP equation is, however, more tractable.

In a local spin-density approximation, $G_{\rm XC}[\vec{r}, \vec{r}'; n]$ is reduced to

$$G_{\rm XC}[\vec{r}, \vec{r}'; n]_L = J(n(\vec{r})) \delta(\vec{r} - \vec{r}') \ , \qquad (22)$$

where

$$J(n) = \chi_{\rm XC}^{-1}(n) - \chi_F^{-1}(n) \ ,$$
$$\chi_{\rm XC}(n) = \chi_{\rm XC}(q = 0; n), \text{ and } \chi_F(n) = \chi_F(q = 0; n) \ . \qquad (23)$$

The long-wavelength limit susceptibility $\chi_{\rm XC}(n)$ is the jellium susceptibility χ_P shown in Fig. 6. The VP theory enables one to pick one of the jellium results, to *dress* it with the band-structure effect using Eqs. (16), (22), and (23), and to compare with the experimental results $\chi_{\rm XCB}(r_s)$.

MacDonald, Perdew, and Vosko[134] recently calculated $\chi_{\rm XCB}/\chi_F$ and $d(\chi_{\rm XCB}/\chi_F)/dr_s$ for Li and Na using the VP theory. They used the *consensus* curves, DG, HO, PTV, VS, L-RPA, BH, HL' in Fig. 6 as $\chi_{\rm XC}(n)$ in Eq. (23). The results are shown in Table II. The reasonable agreement between the experimental and the theoretical values for Li is most encouraging and assures us that the band-structure correction for Na is reliable.

The excellent agreement for Na, therefore, indicates that the *consensus* curves have now acquired a concrete experimental support at least for $r_s \lesssim 4$. This is one of the rare experimental results which can be directly compared with the XC effect for the interacting electron gas in the metallic-density range.

CONCLUSION

The pressure dependence of the Pauli susceptibility in Li and Na yielded the volume dependence of the amplitude of the wave function for conduction electrons. This was compared with theoretical

predictions. The same data revealed that the four experimental values; $(\chi_P/\chi_F)_{\rm Li}$, $(\chi_P/\chi_F)_{\rm Na}$, $[d(\chi_P/\chi_F)/dr_s]_{\rm Li}$, and $[d(\chi_P/\chi_F)/dr_s]_{\rm Na}$, combined with the new general theory by Vosko and Perdew, led to the definitive experimental verification of longstanding theories for the exchange-correlation effect in an electron liquid of metallic density. A comparison between the Li experimental results and calculation strongly supports the validity of the VP scheme, which incorporates exchange-correlation and band-structure effects in the Pauli susceptibility without heuristic assumptions.

APPENDIX

In the Landau theory the effective mass modified by the XC effect and by the band-structure effect $m^*_{\rm XCB}$ is expressed by[135]

$$\frac{m^*_{\rm XCB}}{m^*_B} = 1 + \frac{1}{3} \frac{\Omega}{\pi^2} \frac{m^*_{\rm XCB}}{\hbar^3} P_f f_1^s \ , \qquad (A1)$$

where f_1^s is the Legendre expansion coefficient (for $l = 1$) of the spin-symmetric part of Landau parameter. P_f is the Fermi momentum. When one turns off the band-structure effect in Eq. (A1) assuming that f_1^s is unchanged during process, one gets

$$\frac{m^*_{\rm XC}}{m} = 1 + \frac{1}{3} \frac{\Omega}{\pi^2} \frac{m^*_{\rm XC}}{\hbar^3} P_f f_1^s \ . \qquad (A2)$$

These equations lead to

$$\frac{1}{m^*_{\rm XCB}} - \frac{1}{m^*_{\rm XC}} = \frac{1}{m^*_B} - \frac{1}{m} \ . \qquad (A3)$$

A similar expression for $\chi_{\rm XCB}$ is[136]

$$\frac{1}{\chi_{\rm XCB}} = \frac{m}{m^*_{\rm XCB}} \frac{1}{\chi_F} + \frac{1}{\mu_e^2} f_0^a \ , \qquad (A4)$$

where f_0^a is the first ($l = 0$) Legendre coefficient for the spin-antisymmetric part of the Landau parameter. By turning off the band-structure effect, one obtains

$$\frac{1}{\chi_{XC}} = \frac{m}{m^*_{XC}} \frac{1}{\chi_F} + \frac{1}{\mu^2_e} f^a_0 .$$ (A5)

Again f^a_0 is assumed to be independent of the strength of the band-structure effect. From (A4) and (A5),

$$\frac{1}{\chi_{XCB}} - \frac{1}{\chi_{XC}} = \left(\frac{m}{m^*_{XCB}} - \frac{m}{m^*_{XC}}\right) \frac{1}{\chi_F} .$$ (A6)

By using (A3), Eq. (A6) reduces to

$$\chi_{XCB} = \chi_{XC} \Big/ 1 + \left(\frac{m}{m^*_B} - 1\right) \frac{\chi_{XC}}{\chi_F} .$$ (A7)

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