

ratory<sup>3,8</sup> has given evidence that cracking is effective in relieving surface strain and that it is a rate process. The rate is quite low at room temperature and is accelerated by radiation and mechanical working. The experiments described in the present paper show that cleaved faces require less irradiation to produce significant damage than those which have been water-polished. This fact may be interpreted to mean that the energy density introduced by cleavage is higher in a relatively thin layer at the surface.

The tendency of the crystallites to assume preferred orientations is interesting in light of other work. Linear surface defects formed by irradiation and heat treat-

<sup>8</sup>H. R. Leider and L. A. Girifalco (to be published).

ment of sodium chloride also occurred in preferred directions.<sup>3</sup>

The present study indicates that the predominant orientations have the (100) direction of the crystallites parallel to the cube edge of the substrate and parallel to the diagonal of the substrate. A more extensive analysis of the diffraction patterns is needed to confirm this relationship.

#### ACKNOWLEDGMENTS

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## Electron Spin Paramagnetism of Lithium and Sodium\*

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The paramagnetic susceptibility  $\chi_p^e$  of conduction electron spins is isolated experimentally from the total magnetic susceptibility in metallic lithium and sodium by studying the intensity of the conduction-electron spin resonances. The absolute intensity of absorption is calibrated by comparison with the nuclear resonance of the metal nuclei in the same sample and at the same frequency, the two resonances being observed merely by changing the static magnetic field. In this manner  $\chi_p^e$  is measured in terms of the nuclear static susceptibility,  $\chi_p^n$ , which in turn can be calculated accurately from the Langevin-Debye formula. A narrow band modulation technique gives improved signal to noise over our earlier work. The values of  $\chi_p^e$  are  $(2.08 \pm 0.1) \times 10^{-6}$  cgs volume units for lithium at 300°K and  $(0.95 \pm 0.1) \times 10^{-6}$  cgs volume units for sodium at 79°K, in rather good agreement with the theory of Pines and Bohm, but in substantial disagreement with the simple Pauli model, or the results of Sampson and Seitz. Experimental precision does not permit conclusions to be drawn about the diamagnetism of conduction electrons.

### I. INTRODUCTION

THE static magnetic susceptibility of a metal,  $\chi_0$ , is in general composed of two terms,  $\chi_p$  and  $\chi_d$ ,  $\chi_p$  is the paramagnetic contribution arising from polarization of the conduction electron spin moments.  $\chi_d$  is the diamagnetic contribution arising from the orbital motion of the conduction electrons and of the core electrons of the metal atoms. In practice  $\chi_p$  and  $\chi_d$  are comparable in magnitude. Conventional methods of susceptibility measurement (e.g., via Gouy balance) determine the total magnetic susceptibility,  $\chi_0$ , which is the sum of the various contributions to  $\chi_p$  and  $\chi_d$ , whereas theories of metallic susceptibilities give the various terms separately. Thus a comparison between theory and experiment is unsatisfactory even when numerical agreement is found between theoretical and experimental values of  $\chi_0$ .

Recently the interest in susceptibilities of metals has been revived by the major new advances of Bohm and

Pines<sup>1</sup> in the theory of electrons in metals. Largely as a result of their work, we have been stimulated to isolate experimentally for the first time the spin contribution  $\chi_p$  to the total magnetic susceptibility  $\chi_0$ .<sup>2</sup> One might wonder how it is possible to isolate the spin paramagnetic contribution to  $\chi_0$ , if this cannot be done by conventional techniques. We will work out mathematical details below, but in brief, the technique involves the study of the conduction-electron spin resonance. Since the conduction-electron spin resonance arises solely from the spin magnetization, the presence or lack of spin magnetization determines the strength of the resonance, enabling us to measure  $\chi_p$ . As will be shown below, the integrated area under the conduction-electron absorption curve is proportional to  $\chi_p$  with well-known constants of proportionality. Thus an absolute intensity measurement will determine  $\chi_p$ . Such measurements are always difficult, although for

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<sup>1</sup> D. Bohm and D. Pines, *Phys. Rev.* **82**, 625 (1951); D. Bohm and D. Pines, *Phys. Rev.* **92**, 609 (1953); D. Pines and D. Bohm, *Phys. Rev.* **85**, 338 (1952); D. Pines, *Phys. Rev.* **92**, 626 (1953); D. Pines, *Phys. Rev.* **95**, 1090 (1954).

<sup>2</sup> Schumacher, Carver, and Slichter, *Phys. Rev.* **95**, 1089 (1954).

example Hutchison and Pastor<sup>3</sup> have used this method to measure susceptibilities of metal-ammonia solutions.

The essentially new feature of our technique is to compare the spin resonance of the conduction electrons with the spin resonance of the metal nuclei in the same sample. By varying the static magnetic field  $H_0$ , leaving all circuit and sample parameters unchanged, we plot the resonance absorption first for the electrons (at  $H_0 \sim 5$  gauss) and then for the nuclei ( $H_0 \sim 10\,000$  gauss). The ratio of areas then gives us the ratio of  $\chi_p$  to the nuclear static susceptibility. The latter is given by the well-known Langevin-Debye formula

$$\chi_p^n = N\gamma^2 \hbar^2 I(I+1)/3kT,$$

where  $N$  is the number of nuclei/unit volume,  $\gamma$  the nuclear gyromagnetic ratio,  $I$  the nuclear spin, and  $\hbar$ ,  $k$ ,  $T$  all have their usual meaning. Thus we convert our experiment to a simple comparison of areas.

The first measurements on lithium by Schumacher, Carver, and Slichter<sup>2</sup> have been reported previously. The resonances were observed by using an oscilloscope and photographic technique. In an effort to improve the precision, we have redone and extended those measurements using conventional narrow-band modulation techniques. In this paper we report results for both lithium (at room temperature) and sodium (at liquid nitrogen temperature) obtained by the improved method.

## II. INTEGRAL RELATIONS

The basic equation relating  $\chi_p$  to the resonance absorption is

$$\chi_p = \frac{2\gamma}{\pi\omega} \int_0^\infty \chi'' dH_0, \quad (2)$$

where  $\gamma$  is the (nuclear or electron) gyromagnetic ratio,  $\omega$  the angular frequency of the linearly polarized alternating magnetic field, and  $\chi''$  the imaginary or loss part of the complex magnetic susceptibility. We note that this relation applies to our experimental situation of fixed frequency and variable static field,  $H_0$ . This equation should not be confused with the well-known Kramers-Kronig relation<sup>4,5</sup>

$$\chi_p = - \int_0^\infty \frac{\chi'' d\omega}{\pi\omega}, \quad (3)$$

which involves an integral with respect to frequency.

We now wish to justify Eq. (2). We have been able to do so for various special cases, which fortunately include our experiment. We suspect that justification can be given for more general cases.

It is clear that for a resonance very narrow with respect to the resonant frequency, variation of  $\chi''$  with

$\omega$  will be quite rapid, enabling us to pull  $1/\omega$  outside the integral (3). Then, using the equivalence of field and frequency  $\omega = \gamma H_0$  for resonance, we obtain Eq. (2). So Eq. (2) is satisfactory for narrow lines, the approximation being better the narrower the line. All nuclear resonance lines as normally observed fall into this class. The electron lines, however, are sometimes too broad.

Another case for which we can justify the use of (2) is for solutions of the Bloch<sup>6</sup> equations. In this case we have an explicit expression for  $\chi''$ :

$$\chi'' = \frac{\chi_p \omega T_2}{2} \left[ \frac{1}{1 + (\omega - \omega_0)^2 T_2^2} - \frac{1}{1 + (\omega + \omega_0)^2 T_2^2} \right], \quad (4)$$

where  $\omega_0 = \gamma H_0$ , and  $T_2$  is the familiar transverse relaxation time. Substitution of this expression for  $\chi''$  in (2) and assuming  $T_2$  is constant independent of  $H_0$  gives *exact* verification. It should be pointed out that it is necessary to include the second term in the bracket, often omitted since it is small at resonance, since omission of this term would give a divergent result for the integral.

Equation (4) says that  $\chi''$  vanishes at  $H_0 = 0$ , whereas it should<sup>7,8</sup> reduce to the Debye expression as observed in the classic experiments of Gorter.<sup>9</sup> If we consider cases in which  $T_1 = T_2$ , we should find

$$\chi'' = \chi_p \omega T_1 / (1 + \omega^2 T_1^2), \quad (5)$$

when  $H_0 = 0$ . The low-field difficulty can be remedied in the Bloch equations by saying the spins relax towards a magnetization  $\mathbf{M}_0 = \chi_p (\mathbf{H}_0 + \mathbf{H}_x)$  rather than  $\mathbf{M}_0 = \chi_p \mathbf{H}_0$ , where  $\mathbf{H}_x$  is the applied alternating field. Then we obtain the relation

$$\chi'' = \frac{\chi_p \omega T_1}{2} \left[ \frac{1}{1 + (\omega - \omega_0)^2 T_1^2} + \frac{1}{1 + (\omega + \omega_0)^2 T_1^2} \right], \quad (6)$$

which behaves properly at  $H_0 = 0$ .

To our knowledge the problem of the correct limiting expression was first treated by Kronig<sup>8</sup> actually prior to the first experimental observation of any magnetic resonance in bulk material. He gives Eq. (6). It has since been rediscovered independently by various workers.<sup>7,10</sup> We should remark that one error which appears in the literature is the statement that the Bloch solution is valid as long as  $H_x \ll H_0$ . This statement appears reasonable if one compares the two expressions for  $M_0$ . Actually, however, the condition on validity of the Bloch solution is  $H_0 \gg 1/2T_1$ . When  $H_0$  is large compared to the line width, we are dealing with the case Gorter<sup>9</sup> has termed "transverse," but when

<sup>6</sup> F. Bloch, Phys. Rev. **70**, 460 (1946).

<sup>7</sup> M. A. Garstens, Phys. Rev. **93**, 1228 (1954).

<sup>8</sup> R. de L. Kronig, Physica **5**, 65 (1938).

<sup>9</sup> C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., New York, 1945).

<sup>10</sup> R. K. Wangness, Phys. Rev. **98**, 927 (1955); Codrington, Olds, and Torrey, Phys. Rev. **95**, 607 (1954).

<sup>3</sup> C. A. Hutchison and R. C. Pastor, Revs. Modern Phys. **25**, 285 (1953).

<sup>4</sup> H. A. Kramers, Atti. Congr. fis., Como, 545 (1927).

<sup>5</sup> R. de L. Kronig, J. Opt. Soc. Am. **12**, 547 (1926).

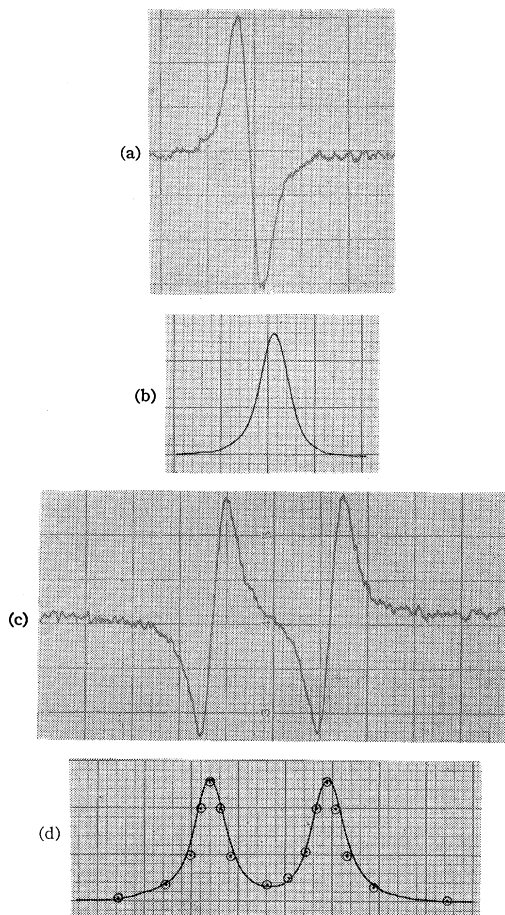


FIG. 1. (a)  $\text{Li}^7$  resonance in Li metal at 10 000 gauss as plotted by recorder. Line width is approximately  $\frac{1}{2}$  gauss. (b) Integral of experimental curve (a) as plotted by the differential analyzer. (c) Electron spin resonance in lithium metal as plotted by recorder. Field sweep is about  $-20$  gauss to  $+20$  gauss. (d) Solid line is integral of experimental curve (c). Circles represent points calculated from Eq. (6) with  $\omega T_1 = 3.5$  and fitted to the peak height. All resonances are at room temperature.

$H_0$  is less than the line width we can no longer distinguish between his "longitudinal" and "transverse" cases. Since the "longitudinal" case obeys a Debye law, we expect the Bloch equations to be valid only for  $H_0$  large compared to  $1/\gamma T_1$ .

The assumption that the spins relax along the *instantaneous* total applied field appears reasonable when the relaxation mechanism is characterized by a correlation time very short compared to the period of the alternating field, since then the field  $\mathbf{H}_0 + \mathbf{H}_x$  is quasistatic during relaxation processes. Of course, the case of such short correlation times also is that for which  $T_1 = T_2$ . The conduction electron relaxation is certainly characterized by such a short correlation time. Experimentally, it has been shown that  $T_1 = T_2$  for the conduction electron resonance.<sup>11</sup> As we antici-

pate, our experimental data fit Eq. (6). The comparison of experimental and theoretical lines for both lithium and sodium is given in Figs. 1 and 2. The method of processing the data is described in Sec. V. We see the theoretical points (circled for ease in reading) fall on the experimental curves.

Substitution of Eq. (6) into (2) verifies that Eq. (2) holds exactly for this line shape also. Once again we assume  $T_1$  to be independent of  $H_0$ , a fact which has been verified experimentally all the way from low fields of several gauss<sup>11</sup> up to several thousand gauss for conduction electrons.<sup>12</sup>

We can conclude by saying our basic expression, Eq. (2), holds for nuclear lines because they are so narrow, and for the electron lines because their line shape is given by Eq. (6). Since we depend less on the details of line shape the narrower the resonance, we are always anxious to get the electron line as narrow as possible.

Using subscripts or superscripts of  $e$  and  $n$  to denote electron or nucleus we find, finally:

$$\chi_p^e = \chi_p^n \frac{\gamma_e \int \chi_e'' dH_0}{\gamma_n \int \chi_n'' dH_0} = \chi_p^n \frac{\gamma_e A_e}{\gamma_n A_n}, \quad (7)$$

where  $A_e$  and  $A_n$  are the areas under the curves of absorption *vs* magnetic field obtained from the same sample without changing circuit parameters in passing from one resonance to the other. Equation (7) now gives us a convenient form to utilize our data in computing  $\chi_p^e$ .

### III. THEORY OF THE EXPERIMENTAL TECHNIQUE

Let us now turn to an analysis of the experimental method. The accuracy of the photographic experiment<sup>2</sup> reported previously was limited by the necessity of using broad band techniques in order to reproduce the exact line shape of the resonances for oscilloscope display. To extend the measurements to sodium, the resonance must be observed at liquid nitrogen temperature where the electron spin resonance is sufficiently narrow.<sup>11,12</sup> At these temperatures the nuclear resonance broadens enough to make the photographic technique somewhat poorer than desirable. Hence we have employed narrow band techniques to repeat the experiment for lithium and to measure the susceptibility in sodium.

The method used to "narrow band" the apparatus is the standard one in magnetic resonance,<sup>13</sup> employing 30-cycle modulation of the magnetic field and detection of the resultant 30-cycle resonant signal by a phase-sensitive "lock-in" detector. For our experiment the

<sup>11</sup> T. R. Carver, thesis, University of Illinois, 1954 (unpublished).

<sup>12</sup> George Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).

<sup>13</sup> Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

output of the lock-in was recorded on a recording millivoltmeter. The aim is to obtain from the recorded output of the lock-in the quantity of Eq. (2):  $\int \chi'' H_0$ . We will perform an analysis of signal from the lock-in, following Andrew.<sup>14</sup> From this analysis we will find that we will need knowledge of  $H_m$ , the modulation amplitude, and  $dH_0/dt$ , the rate at which  $H_0$  is swept through the line. A somewhat surprising consequence will be that our results will be insensitive to modulation broadening of the resonance.

Andrew shows that if one detects the absorption rather than the dispersion, the signal into the lock-in,  $V_{in}$ , may be written

$$V_{in} \propto \chi''(h_1) + \sum_{p=1}^{\infty} \frac{H_m^p \sin^p(\omega_m t)}{p!} \left( \frac{d^p \chi''}{dh^p} \right)_{h_1}, \quad (8)$$

where  $h = (\omega/\gamma) - H_0$ . In the presence of modulation,

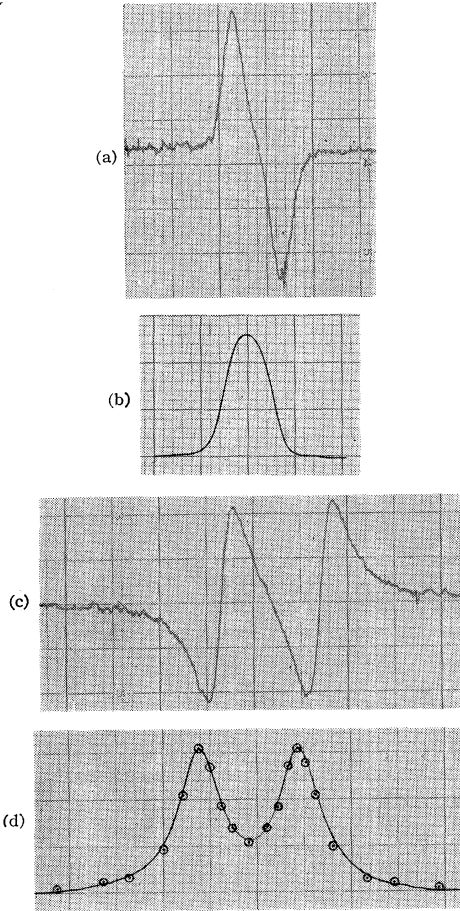


FIG. 2. (a)  $\text{Na}^{23}$  resonance in sodium metal at 10 000 gauss and  $T=79^\circ\text{K}$  as plotted by recorder. Line width is approximately 2.5 gauss. (b) Integral of experimental curve (a) as plotted by the differential analyzer. (c) Electron spin resonance in sodium metal at  $T=79^\circ\text{K}$  as plotted by the recorder. Field range is about  $-20$  gauss to  $+20$  gauss. (d) Solid line is integral of experimental curve (c). Circles represent points calculated from Eq. (6) with  $\alpha = \omega T_1 = 2.1$  and fitted to the peak height.

<sup>14</sup> E. R. Andrew, Phys. Rev. **91**, 425 (1953).

$h$  is written  $h = h_1 + H_m \sin(\omega_m t)$ , where  $h_1$  is the mean value of  $h$ ,  $\omega_m$  is the modulation frequency, and  $H_m$  is the amplitude of the modulation. The expansion (8) in a Taylor's series is valid for values of  $H_m$  of the order of the line width or smaller. The output of the lock-in is proportional to the coefficient of  $\sin(\omega_m t)$  in Eq. (8), which Andrew writes as

$$f(h_1) = \sum_{q=0}^{\infty} \frac{H_m^{q+1}}{2^{2q} q! (q+1)!} \left[ \frac{d^{2q+1} \chi''(h)}{dh^{2q+1}} \right]_{h_1}. \quad (9)$$

The recorder records as a function of time, since its chart mechanism is driven by a synchronous motor. Equation (7) requires the integral with respect to  $H_0$ , or  $h_1$  in the notation above. The proper integral to perform then is

$$\int_0^{\infty} dt \left( \frac{dh_1}{dt} \right) \int_0^t dt' \left( \frac{dh_1}{dt'} \right) f(h_1(t')), \quad (10)$$

where  $f(h_1(t))$  is the function plotted on the chart. This can be seen to yield

$$\begin{aligned} \int_0^{\infty} dt \left( \frac{dh_1}{dt} \right) \int_0^t dt' \left( \frac{dh_1}{dt'} \right) f(h_1(t')) \\ = \frac{H_m}{4} \int_{H_0=0}^{\infty} \chi''(H_0) dH_0. \end{aligned} \quad (11)$$

All higher terms in the series have vanished identically because  $\chi''$  and all its derivatives vanish for  $H_0=0$  and  $\infty$  for the nuclear resonance. For the electron resonance, with an appreciable zero field absorption, odd order derivatives vanish at  $H_0=0$  due to the symmetry of  $\chi''$  about  $H_0=0$ , and of course the absorption and all derivatives vanish at  $H_0=\infty$  also. If  $dh_1/dt$  is constant, the desired integral is proportional to

$$\int_0^{\infty} \chi''(H_0) dH_0 \sim \frac{1}{H_m} \left( \frac{dh_1}{dt} \right)^2 \int_0^{\infty} dt \int_0^t dt' f(h_1(t')). \quad (12)$$

Equation (12) implies that we must measure both  $H_m$  and  $dh_1/dt$  on the same relative scale for both the electron and nuclear resonances, and it tells us that as long as  $H_m$  is small enough that the Taylor expansion (8) is valid, we need not concern ourselves with the possibility of distorting the line by too large modulation. That only the first term of the series (9) remains after the double integration is a fortunate simplification. We also see that to integrate the recorded curves directly it is necessary to keep  $dh_1/dt$  constant.

#### IV. APPARATUS

The measurements were performed at 17.4 Mc/sec for lithium and 11.5 Mc/sec for sodium. The generation of the rf voltage, indicated schematically in Fig. 3, was

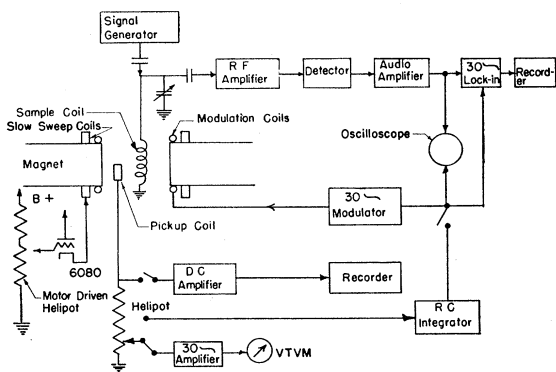


FIG. 3. Block diagram of the apparatus.

done by a simple battery powered triode oscillator at the higher frequency, and by a Hewlett-Packard Model 608D VHF Signal Generator at both frequencies. Because a bridgeless technique for detecting the nuclear signal was used, considerations of oscillator noise were of prime importance. Although it was found that the Model 608D was slightly noisier, it was used for most of the runs for convenience. The internal amplitude modulation provisions were found convenient for gross tuning adjustments, and the calibrated attenuator on the output of the instrument made relative measurements of the voltage applied to the sample coil simple and accurate.

Great stability was required of the rf circuits. For this reason and because of uncertainty of tuning, bridge circuits were considered and abandoned. Most desirable would be spectrometer circuits of the type described by Pound<sup>15</sup> or Gutowsky.<sup>16</sup> These circuits are stable and have the desirable property that they detect only  $\chi''$ . Unfortunately these circuits typically run at somewhat higher rf levels than it was possible to use in the experiment, because no detectable degree of saturation could be allowed. In order to eliminate instability due to warm up problems, the circuits were kept warm between runs by a commercial power supply. For the actual data runs all the amplifiers preceding the lock-in were switched to batteries. The circuits chosen allowed data to be taken over as wide a range of rf voltage on the sample coil as desired.

The tuned sample tank circuit was followed by one or two stages of tuned rf amplifiers with gain ranging from 10 to 400. The number of stages used was determined by the voltage level at the sample tank, since it was desired to work at all times with approximately the same amplitude of rf at the grid of the detector. The detector was of standard plate detector design. The tuned circuits preceding the detector were tuned to maximize the dc current through the detector. A maximum could be detected in a sensitive manner by a

<sup>15</sup> R. V. Pound and W. D. Knight, Rev. Sci. Instr. 21, 219 (1949).

<sup>16</sup> Gutowsky, Meyer, and McClure, Rev. Sci. Instr. 24, 644 (1953).

differential voltmeter at the cathode of the detector tube.

A standard analysis of the rf circuits, similar to the analysis of Pake,<sup>17</sup> shows that the output of the detector varies linearly with  $\chi''$  if the sample circuit is tuned to give a maximum rf at the detector. If, as must necessarily occur in practice, the tank condenser is imperfectly tuned, deviating an amount  $\Delta C$  from its proper value  $C_0$ , the resonance signal from the apparatus will be proportional to

$$\chi'' - 2Q(\Delta C/C_0)\chi'. \quad (13)$$

$Q = R/\omega L$  is the conventional "Q-factor" for a parallel RLC resonant circuit. The integration of this signal, which is the quantity of interest to this experiment, yields just  $\int_0^\infty \chi'' dH_0$  for the case of the nuclear line, since  $\int_0^\infty \chi' dH_0 = 0$  is an excellent approximation for this case. For the electron resonance, using the form of  $\chi'$  predicted by the modified Bloch equations<sup>7,10</sup>

$$\int_0^\infty \chi' dH_0 = \frac{\omega \chi_p}{\gamma} \left[ \frac{1}{\alpha^2} - \frac{1}{3\alpha^4} + \dots \right], \quad (14)$$

for  $\alpha > 1$ , where  $\alpha \equiv \omega T_1$  is a parameter characterizing the sharpness of the resonance. The factor  $2(\Delta C/C)Q/\alpha^2$  was estimated always to be  $< 1/10$  for  $\alpha = 2$  by experience with the "feel" of the tuning. Since the sign of  $\Delta C$  was random, the average value of the parameter multiplying  $\chi'$  should be zero over a large number of runs. A check on the effect of  $\chi'$  was provided by the consistency of the value of zero-field absorption for the electron resonance, since the mixing in of  $\chi'$  will alter this from the value for  $\chi''$  alone. The zero-field absorption for sodium was particularly sensitive to this check since for our experiments  $\alpha = 2.1$  for sodium whereas  $\alpha = 3.5$  for lithium. Over approximately 25 runs the value of the zero-field absorption in percent of peak signal was  $37 \pm 5$  percent. This value was checked by using a spectrometer which measures only  $\chi''$ , kindly loaned by Professor H. S. Gutowsky of the Department of Chemistry and agreement was found. The spread in zero-field absorption for the experimental runs turns out to be no greater than was found with several runs with the spectrometer.

The audio-amplifiers are of standard design and of sufficient gain such that reasonably strong resonant signals could be displayed on a DuMont 304 oscilloscope. The lock-in circuit is taken from a design by Shuster<sup>18</sup> and is preceded by a 30-cycle twin tee amplifier of standard design. The output of the lock-in is recorded by a Leeds and Northrup Speedomax 0-10 mv recorder.

The static magnetic field  $H_0$  was provided by an electromagnet with the current provided by a regulated power supply, designed for the most part by Mr. H. W. Knoebel. The power supply provides maximum

<sup>17</sup> G. E. Pake, Am. J. Phys. 18, 473 (1950).

<sup>18</sup> N. A. Shuster, Rev. Sci. Instr. 22, 254 (1951).

current of 5 amperes at 1000 volts to the main coils. This yields a maximum field of 10 600 gauss. The power supply is current regulated against slow drifts in current and voltage regulated against fast variations. At its best the magnetic field was stable to one part in  $10^6$  over periods of a few minutes.

The slow sweep of the "static" field  $H_0$  was provided by two 2000-ohm coils placed around the iron near the pole faces. These were placed in the cathode of a 6080 vacuum tube whose plate was tied to  $B+$  and whose grid voltage was obtained from a motor-driven helipot connected between ground and a variable resistor connected in turn to  $B+$ .  $dH_0/dt$  was measured from the output of a pickup coil placed in the magnet gap as close to the sample as possible. This output was preamplified by a Leeds and Northrup dc "chopper" amplifier and recorded on a Brown 0-10 mv recorder. This furnished the value of  $dH_0/dt$  on a relative scale as needed in Eq. (12). Equation (12) also requires that  $dH_0/dt$  be constant. The operator was able to monitor  $dH_0/dt$  by observing the pickup voltage on the Brown recorder. By varying the value of the resistance between the helipot and  $B+$  he could correct for any small nonlinearities in  $dH_0/dt$ . In addition, since a record of  $dH_0/dt$  was provided, a run could be eliminated if the sweep rate was not satisfactory. This method was found to be simple and satisfactorily effective.

The 30-cycle modulation of the field was accomplished by separate 1.8-ohm coils wound at the edges of the pole faces and driven from the output transformer of the standard 30-cycle modulator. Equation (12) requires that the amplitude of the 30-cycle component of the modulation be known on some relative scale. To measure  $H_m$  without error from meter non-linearity, a known and adjustable fraction of the pick-up voltage from the gap coil was tapped off by a helipot, amplified by a 30-cycle tuned amplifier, and fed into a VTVM. The helipot was adjusted to produce a standard VTVM reading, so that relative values of  $H_m$  were given by the relative helipot settings.

The apparatus used in the experiment described previously<sup>2</sup> is shown also in Fig. 3. The only modulation of the field was provided by a Variac rather than by the modulator and slow sweep, and the known fraction of the pickup coil voltage was integrated by the  $RC$  integrator and applied to the  $x$ -axis of the oscilloscope as described in the earlier letter.

For sodium the experiments were conducted at liquid nitrogen temperatures. Simple cryogenic apparatus was constructed from "floralfoam." Briefly, the glass vial containing the sample rested on a brass bar which dipped into liquid nitrogen contained in a cavity scooped from floralfoam. Above the small metal sample box was another floralfoam vessel containing liquid nitrogen. The upper "Dewar" had a slow leak which allowed the nitrogen to flow over the sample box and to keep the lower Dewar full. The temperature, as

read by a thermocouple attached to the glass vial, was found to remain at 79°K as long as the upper Dewar was kept filled.

The sample preparation has been described<sup>19</sup> in another publication from this laboratory. It is important that the particle size be small compared to skin depth in the metal at the frequencies and temperatures at which the experiment was conducted. The lithium particles averaged 15 microns in diameter and the sodium particles from 3 to 10 microns. These sizes are small enough so that the effects reported by Feher<sup>12</sup> and explained by Dyson<sup>20</sup> are safely absent.

#### V. EXPERIMENTAL PROCEDURE AND ANALYSIS OF RESULTS

In this section we will describe the experimental procedure and the method of analysis of data. A typical run involved the following procedure. As already mentioned, the rf circuits, detector, and audio amplifier were kept at thermal equilibrium by a commercial power supply between runs. Approximately half an hour before a run was to start, they were converted to batteries, and allowed to reach equilibrium again. During this time the sample tank circuit and rf amplifier were tuned and retuned. With the magnet on, the slow sweep mechanism was swept from about  $-20$  gauss to  $+20$  gauss and the electron resonance was recorded. During this time  $dH_0/dt$  was recorded. After recording the modulation voltage from the reading on the helipot necessary to produce four volts rms on the VTVM at the output of the 30-cycle amplifier, the magnetic field was changed to slightly over 10 000 gauss. The nuclear resonance, modulation amplitude, and  $dH_0/dt$ , were recorded as in the electron case. In the case of lithium, another nuclear resonance was immediately recorded, usually with different modulation amplitude, and then another electron resonance was recorded. In the case of sodium, the rf amplifiers and the sample tank circuit were retuned before the second nuclear and electron resonances in order that the data might represent the largest number of values of  $\Delta C$ , the "detuning" capacity defined in Eq. (13). For sodium  $\alpha=2.1$  as compared to 3.5 for lithium, so  $\Delta C$  was somewhat more important for sodium.

The data was integrated in a one-step process by the Nordsieck differential analyzer. This instrument makes it possible to plot the first integral of the experimental curve and at the same time record a number representing the second integral. Care was necessary in the selection of the base line in order that the integral converge. It was found that it was necessary to select the baseline empirically within the noise, as variations within noise of the supposed base line could mean the difference between convergence of the integral and a first integral which does not return to zero off the

<sup>19</sup> D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

<sup>20</sup> Freeman J. Dyson, Phys. Rev. **98**, 349 (1955).

resonance. Once a baseline was selected the area under the first integral could be reproduced within one percent. From the relative areas of the resonances, the relative modulation amplitudes, the recorded  $dH_0/dt$ , and the nuclear susceptibility calculated from the Langevin-Debye formula and known isotope abundance, a value of the electron paramagnetic susceptibility for lithium was calculated from an arithmetic average of the two nuclear and two electron resonances. This value is termed the result of a "run." For lithium we have taken 21 such runs for sample 1 and 8 runs for sample 2. For sodium, because of the greater effect of an imperfectly tuned sample tank on the electron resonance area, the results of the two (or occasionally more) nuclear lines were averaged arithmetically and two values of the susceptibility were calculated from this average nuclear area and from the two electron areas which were taken under different tuning conditions. The sodium value represents the results from 25 such electron areas. In addition, runs were taken over a wide range of rf voltages on the sample coil in order that it be clear that the final results do not represent the effects of saturation of the nuclear resonance. Figure 1 shows the recorder traces for the nuclear and electron resonances for lithium, with the associated first integral obtained directly from the differential analyzer. The noise on the experimental curve was followed closely during the integration process. It is interesting to note the relative absence of noise on the integrated curve. Figure 2 shows the corresponding curves for sodium.

Effects of impurities in the sample on the experiment fall into two general classes: impurities affecting the nuclear resonance and paramagnetic or ferromagnetic impurities affecting the electron spin resonance. Since the theory of the measurement requires the assumption of one conduction electron per nucleus (apart from the isotope abundance correction), the presence of a non-metallic lithium compound would possibly enhance the nuclear resonance anomalously. However, the magnitude of the external magnetic field at which the nuclear resonance occurs differs for nuclei in nonmetallic surroundings from the resonance field for metallic nuclei due to the well-known Knight shift. For  $\text{Li}^7$  the shift is about 2 gauss at  $H_0=10\,000$  gauss, and for  $\text{Na}^{23}$  it is about 10 gauss at  $H_0=10\,000$  gauss. Both these shifts are large compared to the line widths of the respective resonances, so that had nuclei in nonmetallic compounds been present, they would have been removed from contributing to the "metal" line.

TABLE I. Summary of experimental data.

Sample	Method	Temperature	$\chi_p^e$ (cgs volume units $\times 10^6$ )
Li 1	Oscilloscope	Room temperature	2.0 $\pm$ 0.3
Li 1	Lock-in	Room temperature	2.08 $\pm$ 0.1
Li 2	Lock-in	Room temperature	2.09 $\pm$ 0.15
Na	Lock-in	Liquid $\text{N}_2$	0.95 $\pm$ 0.1

TABLE II. Theoretical<sup>a</sup> and experimental values of  $\chi_p^e$  (cgs volume units  $\times 10^6$ ).

Metal	Experimental value	Pauli <sup>b</sup>	Sampson and Seitz <sup>c</sup>	Pines <sup>d</sup>
Lithium	2.08 $\pm$ 0.1	1.17	2.92	1.87
Sodium	0.95 $\pm$ 0.1	0.64	1.21	0.85

<sup>a</sup> All theoretical values use  $m^*/m=1.46$  for Li and  $m^*/m=0.985$  for Na. These values are due to H. Brooks.

<sup>b</sup> See reference 21.

<sup>c</sup> See reference 23.

<sup>d</sup> D. Pines, Phys. Rev. **95**, 1090 (1954).

Paramagnetic and ferromagnetic impurities in the sample might contribute to the electron resonance in such a way as to yield an anomalously high value for the susceptibility. This effect resembles the effects of these impurities on the static balance measurements of  $\chi_0$ . However, many types of these impurities can be eliminated as producing no effect. Observed ferromagnetic resonances, which are several hundred gauss broad, are too wide to be seen with our apparatus and will give no error. Any impurity, whether in the oil in which the metals were dispersed, or in the metal itself, which exhibits a hyperfine interaction would, in the weak fields used for the electron resonance, be removed in resonant frequency from the free-electron value. In addition, any fixed electron spin in the metallic lattice would have a line width equal to or greater than the rigid lattice line width for the nuclear resonance: three gauss for sodium, six gauss for lithium. These minimum line widths are greater than the observed two to three gauss electron resonances for lithium and about equal to the sodium electron resonance widths. In addition, any electronic impurity with a relaxation time less than or equal to  $10^{-9}$  second would have too broad a resonance to be observed. For any impurity to make a major contribution to our results it would have to have a line width and shape very close to the widths and shapes of the conduction electron resonances themselves, since, as shown in Figs. 1 and 2, the experimental line shapes correspond quite closely to the predicted shapes. In support of the above arguments for lithium, we can report no sample dependence in the susceptibility for the two samples checked. A further check would be the observation of the temperature dependence of the susceptibility, since the conduction electron susceptibility is temperature independent, contrary to expectations for a paramagnetic impurity susceptibility. Such checks are being considered for the future.

## VI. RESULTS AND CONCLUSIONS

The results for  $\chi_p^e$  are listed in Table I. The two lithium samples were chosen because they differ in the width of the conduction electron line, but it is seen that the value of  $\chi_p^e$  is sample-independent.

No systematic difference is found in going from the oscilloscope to the lock-in technique. The lock-in value for Li 1 (Fig. 1) is the result of twenty-one runs. Only

TABLE III. Experimental estimates of  $\chi_D$  (cgs volume units  $\times 10^6$ ).

Metal	$\chi_0$	$\chi_{\text{ion}}$	$\chi_D^{\text{exp}}$	$\chi_D^{\text{th}}$
Lithium	$1.89 \pm 0.05^a$	$-0.05^c$	$-0.18 \pm 0.15$	$-0.20^d$
Sodium	$0.70 \pm 0.03^b$	$-0.18^c$	$-0.07 \pm 0.11$	$-0.24^d$

<sup>a</sup> See reference 24.<sup>b</sup> See reference 25.<sup>c</sup> J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932).<sup>d</sup> D. Pines, Solvay Conference Report, 1954 (unpublished).

four of the runs gave values significantly outside the rms error quoted. The lock-in results for Li 2 result from eight runs. The larger rms error results partly from the smaller number of runs, and partly because the electron line in Li 2 was 25% broader. It is believed that the Li electron line width is determined by scattering from impurities. The scattering does not require the impurity to be paramagnetic, and in general it will not be. Thus we do not expect an impurity resonance.

The data for Na, taken at liquid nitrogen temperature to narrow the electron line, result from twenty-five runs. The quoted limit of error is slightly larger than the actual rms deviations.

Table II gives a comparison with the theoretical values obtained from the Pauli theory<sup>21</sup> (corrected for effective masses  $m^*/m$  of 1.46 for lithium and 0.985 for sodium<sup>22</sup>), the theory of Sampson and Seitz,<sup>23</sup> and that of Pines.<sup>1</sup> We see that the agreement is best with the value of Pines, his theoretical values falling a bit below the experimental. The disagreement with Pines is probably not significant, although we believe the disagreement with the Pauli and the Sampson and Seitz values must be considered real.

From the measured values of  $\chi_0$  together with our values of  $\chi_p^e$  we can determine the diamagnetic contribution. Actually, we shall take the theoretical ion-core values,  $\chi_{\text{ion}}$ , as being reliable, and compute values of  $\chi_D$ , the diamagnetism from the conduction electron motion, using  $\chi_d = \chi_D + \chi_{\text{ion}}$ . Unfortunately there is a wide range of experimental values of  $\chi_0$  from which to choose. In the absence of any better criterion, we shall use the latest values of Pugh and Goldman<sup>24</sup> for lithium and those of Bowers<sup>25</sup> for sodium. The theoretical values are due to Pines. The results are given in Table III. It is not clear whether or not there is agreement between theory and experiment for  $\chi_D$ .

Studies of the Knight shift in metals give us experi-

<sup>21</sup> F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).<sup>22</sup> Values of effective mass for lithium and sodium from Harvey Brooks, private communication to D. Pines.<sup>23</sup> J. B. Sampson and F. Seitz, *Phys. Rev.* **56**, 633 (1940).<sup>24</sup> W. Pugh and J. E. Goldman, *Phys. Rev.* **99**, 1633(E), 1641(A) (1955).<sup>25</sup> R. Bowers, *Phys. Rev.* **99**, 1640(A) (1955).TABLE IV.  $\chi_p^e$  from Knight shift data.

Metal	Theoretical $P_F/P_A$	Knight shift $\chi_p^e$	$\chi_p^e$ (This research)
Lithium	$0.49 \pm 0.05^a$	$1.85 \pm 0.20^a$	$2.08 \pm 0.1$
Sodium	$0.80 \pm 0.03^b$	$0.83 \pm 0.03^b$	$0.95 \pm 0.1$ (79°K)

<sup>a</sup> See reference 27.<sup>b</sup> See reference 28, 300°K.

mental values of the product  $\chi_p^e P_F/P_A$ .  $P_F$  is the average value of  $|\psi(0)|^2$  at the Fermi surface,  $\psi(0)$  being the electron wave function at a nucleus.  $P_A$  is the value of  $|\psi(0)|^2$  for a free atom (which can be determined spectroscopically). Townes, Herring and Knight,<sup>26</sup> Kohn,<sup>27</sup> and Kohn and Kjeldaa<sup>28</sup> have computed  $P_F/P_A$ . We may use their data with the experimental Knight shift data of McGarvey and Gutowsky<sup>29</sup> to give an independent value of  $\chi_p^e$ . The results are given in Table IV. The values of  $\chi_p^e$  obtained from Knight shift experiments plus theoretical  $P_F/P_A$  fall slightly below the experimental values, but there is no serious disagreement.

It therefore appears that our experimental results confirm the susceptibility calculations of Pines, and are in substantial agreement with the theoretical results of  $P_F/P_A$ .

The resonance method we have used is unfortunately not applicable to a wide variety of metals since the conduction-electron spin resonance has been found only in the alkali metals and in Be. It may be that other resonances will be found in very pure samples at low temperatures. It will also be worthwhile to extend the measurements on lithium and sodium over a wide temperature range since  $\chi_p^e$  should be independent of temperature, whereas any paramagnetic impurity would presumably obey a Curie's law ( $1/T$ ) dependence.

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<sup>26</sup> Townes, Herring, and Knight, *Phys. Rev.* **77**, 852 (1950).<sup>27</sup> W. Kohn, *Phys. Rev.* **96**, 590 (1954).<sup>28</sup> T. Kjeldaa, Jr., and W. Kohn, *Phys. Rev.* **99**, 622(A) (1955); **101**, 66 (1956).<sup>29</sup> B. R. McGarvey and H. S. Gutowsky, *J. Chem. Phys.* **21**, 2114 (1953).



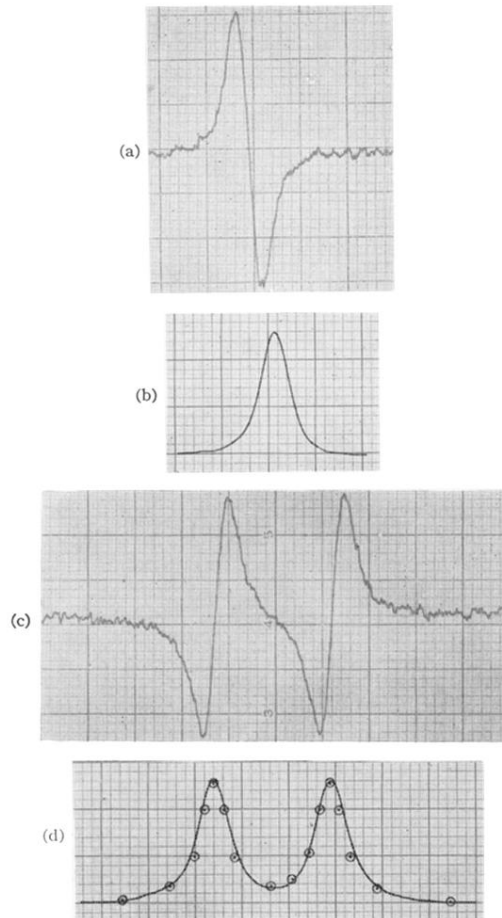


FIG. 1. (a)  $\text{Li}^7$  resonance in Li metal at 10 000 gauss as plotted by recorder. Line width is approximately  $\frac{1}{2}$  gauss. (b) Integral of experimental curve (a) as plotted by the differential analyzer. (c) Electron spin resonance in lithium metal as plotted by recorder. Field sweep is about  $-20$  gauss to  $+20$  gauss. (d) Solid line is integral of experimental curve (c). Circles represent points calculated from Eq. (6) with  $\omega T_1 = 3.5$  and fitted to the peak height. All resonances are at room temperature.

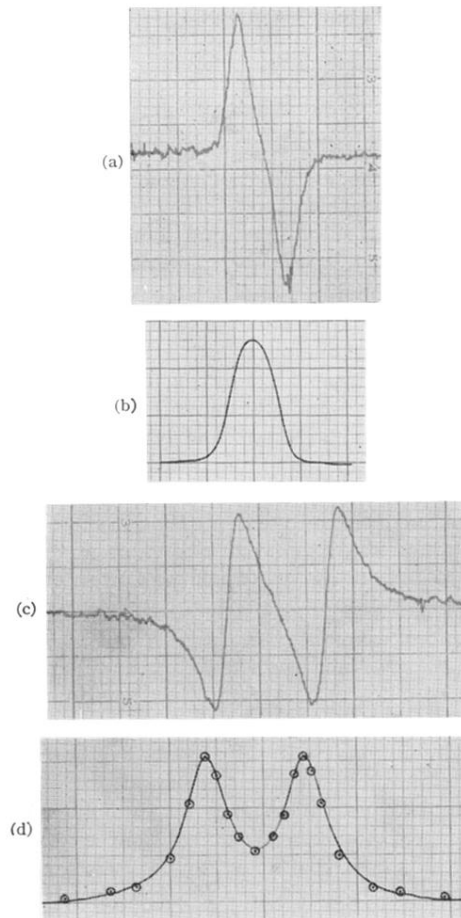


FIG. 2. (a)  $\text{Na}^{23}$  resonance in sodium metal at 10 000 gauss and  $T=79^\circ\text{K}$  as plotted by recorder. Line width is approximately 2.5 gauss. (b) Integral of experimental curve (a) as plotted by the differential analyzer. (c) Electron spin resonance in sodium metal at  $T=79^\circ\text{K}$  as plotted by the recorder. Field range is about  $-20$  gauss to  $+20$  gauss. (d) Solid line is integral of experimental curve (c). Circles represent points calculated from Eq. (6) with  $\alpha=\omega T_1=2.1$  and fitted to the peak height.