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Measurement of the Pauli susceptibility of sodium and lithium*†

B. R. Whiting, N. S. VanderVen, and R. T. Schumacher
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
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The Pauli susceptibility χ_P of sodium and lithium was measured by the magnetic resonance method of Slichter and Schumacher. Analysis of the experiment in terms of linear response theory has established the validity of the method on very general grounds, requiring only that the spectrum of internal fluctuations be independent of the external field, a condition confirmed by detailed analysis of our data. Improved apparatus and data analysis resulted in significantly greater precision than in previous applications of the method. The results are $\chi_P = (1.092 \pm 0.012) \times 10^{-6}$ cgs volume units for sodium at 77 K and $\chi_P = (2.165 \pm 0.039) \times 10^{-6}$ cgs volume units for lithium at 295 K. These are in reasonable agreement with recent theoretical calculations and with values of χ_P inferred from other measurements.

I. INTRODUCTION

There is considerable interest in the Pauli susceptibility of a metal because it is enhanced significantly by electron-electron interactions while being relatively unaffected by electron-phonon processes. Comparing values for theoretical models with the results of experiment allows a straightforward test of the understanding of the role electron-electron interactions play in determining the properties of metals. Recently, while there has been much activity in calculations and measurements of the susceptibility for the simplest metals (the alkalis), unfortunately the uncertainties and discrepancies in the experimental values have been too great to permit any definite conclusions about the accuracy of the calculations. We report here a remeasurement with greatly improved accuracy of the susceptibility of sodium and lithium that permits a more exact test of theory.

In assessing the accuracy of the experimentally determined susceptibility, two factors must be considered. Obviously there will be scatter in the data introduced by a finite signal-to-noise ratio, which leads to imprecision in the final value. Just as important is the uncertainty introduced by a given experimental technique. For example, the Pauli susceptibility can be inferred from measurements of the total susceptibility by subtracting out contributions from the ion cores and Landau diamagnetism, but the uncertainty in these terms is rather large. Likewise, spin-wave measurements[1] involve fitting complex line shapes to determine parameters for the electron-electron interaction and combining them with a proper effective mass. The uncertainty in the effective mass can be large and there is always the question of how accurately the theory describes the experimental lines. Similar problems arise in obtaining χ_P from de Haas-van Alphen measurements,[2] from the application of Korringa relationships,[3] or from measurements of spin-diffusion coefficients.[4] Thus, even if a technique has a fairly high experimental precision, one must still consider the uncertainty of the technique itself.

Our experiment uses the Slichter-Schumacher[5] technique of measuring the susceptibility by finding the area under a magnetic-resonance absorption curve and calibrating the conduction-electron susceptibility in terms of the accurately known nuclear susceptibility. We will show below that this technique determines the susceptibility in a very straightforward manner and has much less uncertainty than other methods. An experimental system is described which significantly improves the signal-to-noise ratio over that of earlier workers. We then discuss the results of this experiment and compare them with theory and other measurements.

II. THEORY OF THE MEASUREMENT

If a system is linear and causal, the real and imaginary parts of its response are related by the Kramers-Kronig[6] integral equations. These give the static susceptibility in terms of a weighted frequency integral of the imaginary part of the dynamic susceptibility

$$\chi(0) = \frac{1}{\pi} \int_{-\infty}^{\infty} [\chi''(\omega)\, d\omega]/\omega \, . \tag{1}$$

In the presence of large fields or for certain explicit line shapes, Eq. (1) can be written as a field integral by making use of the symmetric role of the field and frequency in the resonance condition ($\omega = \gamma H$) of the spin system[7]:

$$\chi(0) \approx (\gamma/\omega\pi) \int_{-\infty}^{\infty} \chi''(H)\, dH \, . \tag{2}$$

Now the voltage $V(H)$ measured from a magnetic resonance spectrometer is proportional to χ'', so a knowledge of the proportionality constant and $V(H)$ would allow a calculation of $\chi(0)$. Unfortunately, the proportionality constant cannot be determined very precisely as it depends on electronic gains, amount of sample, and coil Q, and hence susceptibility measurements using Eq. (2) would not have great accuracy. Slichter and Schumacher overcame this difficulty by replacing this absolute measurement by a relative one. They measured the conduction-electron spin resonance (CESR) and the nuclear spin resonance in a sample with the same spectrometer operating at constant frequency, varying only the field. Since the nuclear susceptibility is given accurately by the Langevin formula,

$$\chi_n = (N/V)\,[\gamma^2\hbar^2 I(I+1)/3kT] \tag{3}$$

the electron susceptibility can be "calibrated" by it and is found to be

$$\chi_e = \chi_n(\gamma_e/\gamma_n)\left(\int V_e(H)\,dH \Big/ \int V_n(H)\,dH\right). \tag{4}$$

Such a ratio measurement can be made with high precision, limited only by the signal-to-noise ratio.

While this method has been used by several groups,[5,8,9] there have been two uncertainties associated with it. First, there is the question of the exactness of Eq. (2), and second, there is the difficulty of including all the area under an absorption line, especially for the CESR line, which has broad wings. We will show below that Eq. (2) is in fact very general. By studying the origins of the line shapes and carefully examining the experimental lines, we will see that a proper data analysis can lead to an accurate area measurement. Thus the experimental technique is found to be on very firm ground.

Equation (2) can be derived by calculating the response of a spin system through the fluctuation-dissipation theorem.[10] This theorem states that the energy absorption (dissipation) of a spin system is related to the Fourier transform of the spin autocorrelation function (fluctuation). The admittance of the spin system can be written as

$$\chi(\omega) = \chi(0) + \frac{i\omega}{h}\int_{-\infty}^{\infty} \langle[\mu(t),\mu(0)]_-\rangle e^{-i\omega t}\,dt, \tag{5}$$

where $\langle\ldots\rangle$ represents traces in a canonical ensemble. For linearly polarized radiation and at high temperatures ($h\omega \ll kT = 1/\beta$), the absorption becomes[11]

$$\chi''(\omega) = \frac{\omega\beta}{4}\int_{-\infty}^{\infty} [\langle\mu(t)\,\mu(0) + \mu(-t)\,\mu(0)\rangle]\,e^{-i\omega t}\,dt. \tag{6}$$

We now must write the equation of motion for the spins, which will have the general form

$$\mu(t) = \mu(0)\exp\left(-i\omega_0 t - i\int_0^t \Delta\omega(t')\,dt'\right). \tag{7}$$

Here, $\omega_0(=\gamma H)$ represents the effect of the external field with all linear effects (e.g., demagnetizing factors, Knight shift) taken into account, and determines the resonance condition. $\Delta\omega$ reflects the internal state of the system, the variation and modulation of the effective field seen by each spin, and corresponds experimentally to the linewidth. In order to justify Eq. (2), we assume that the spectrum of internal fluctuations is independent of the external field $[\Delta\omega \neq f(H)]$. This has been verified experimentally for conduction electrons[12] and for nuclei,[13] and is expected theoretically if the thermal energy is much greater than the Zeeman energy ($\mu H \ll kT$). With this assumption, the equation of motion for a spin can be separated into factors that involve only the internal fluctuations or the external field[14]

$$\mu(t) = \mu^i(t)\,e^{-i\omega_0 t} \tag{8}$$

and Eq. (6) becomes

$$\chi''(\omega) = \frac{\omega\beta}{4}\int_{\infty}^{\infty} \langle\mu^i(t)\mu^i(0)\rangle \times (e^{-i\omega_0 t} + e^{i\omega_0 t})\,e^{-i\omega t}\,dt, \tag{9}$$

since $\langle\mu^i(t)\,\mu^i(0)\rangle = \langle\mu^i(-t)\,\mu^i(0)\rangle$. Substituting this into the Kramers-Kronig relation, one finds

$$\chi_0 = \frac{\beta}{4\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \langle\mu^i(t)\mu^i(0)\rangle(e^{-i\omega_0 t} + e^{i\omega_0 t})\,e^{-i\omega t}\,dt\,d\omega = \beta\langle\mu^i(0)\,\mu^i(0)\rangle. \tag{10}$$

This gives χ_0 in the standard form of a trace over all spins. However, because the field and frequency enter into Eq. (9) only in the symmetric form $(\omega \pm \omega_0)$, one can get an equivalent result in Eq. (10) by changing the variable of integration to give the expression

$$\chi_0 = \frac{\beta}{4\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \langle\mu^i(t)\,\mu^i(0)\rangle(e^{-i\omega_0 t} + e^{i\omega_0 t})\,e^{-i\omega t}\,dt\,d\omega_0 = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\chi''(\omega_0)}{\omega}\,d\omega_0 = \frac{\gamma}{\omega\pi}\int_{-\infty}^{\infty} \chi''(H)\,dH. \tag{11}$$

Equation (2) should therefore be valid for any system that has the characteristics assumed in the derivation: (i) the system must be linear (experimentally, no saturation or skin-depth effects); (ii) the experiment must be in the high-temperature regime ($h\omega, \mu H \ll kT$). Fulfillment of these conditions can be determined by careful examination of the experimental data and departure from these conditions was found to be insignificant to within the accuracy of the measurement. Equation (2) may be thought of as a generalized sum rule for the strength of the spin moments of such a system and should be very accurate for both conduction electrons and nuclei in an alkali metal.

To get the utmost accuracy from the Slichter-Schumacher technique, all the area under the resonance curve must be included in the integral. If a line shape has broad wings, it may be experimentally prohibitive to do this directly, and several measurements[5,9] have neglected to account at all for the CESR wings. Vehse[8] overcame this problem by assuming a Lorentzian line shape for the CESR and correcting his measured area by a factor to account for the wings. The analysis in the present research involved fitting the CESR directly to a Lorentzian line shape and determining the area from the parameters of the fit. This raises the question of how accurately the experimental CESR line is described by a Lorentzian shape.

In order to include 99% of the area under a Lorentzian, one must go approximately 60 halfwidths ($60\ \delta\omega$) into the wings. Thus, to use this technique accurately we require that the line shape be Lorentzian for more than $60\ \delta\omega$. Of course, a Lorentzian absorption line implies an exponential spin correlation function, i.e., the spin correlations must be random in time. Our requirement on the line shape can be stated as a requirement that the correlation function be exponential on a time scale greater than $(60\ \delta\omega)^{-1}$. For our experimental conditions, this means that an electron's environment cannot be strongly correlated over distances which an electron on the Fermi surface can travel in this time (~5000 ions), which is certainly reasonable for the alkali metals where interactions are screened within several ionic distances.

There are two mechanisms that determine the spin correlation function—nonsecular broadening due to interruption of spin phases and secular broadening due to modulation of the frequency of the spin precession. Pines and Slichter[15] have treated the correlation function in terms of a random-walk problem characterized by the ratio of strength of any broadening process to its duration, with small ratios giving narrowed line shapes of Lorentzian form. Using their approach, ratios for the most likely CESR broadening processes—impurity scattering, surface relaxation, phonon spin-orbit coupling—were estimated. When these ratios were used in line-shape calculations based on a model by Anderson,[16] it was found that the CESR lines would be described very accurately by a Lorentzian.[17] In fact the strongest verification of the Lorentzian form of CESR line shape was the excellent fits obtained for the experimental lines which indicate that deviations were smaller than the random noise in the data.

In summary, we have shown that this experimental technique is straightforward, based on reasonable assumptions, and can be used with confidence with an expected systematic uncertainty that is much less than the experimental scatter.

III. EXPERIMENTAL DETAILS

A "Q"-meter spectrometer (shown in Fig. 1) was used because of its simplicity and lack of signal distortion. Briefly, a crystal-controlled oscillator of 19 MHz and very stable amplitude (<10-ppm variation during a measurement lasting 10 min) supplied a constant rf current to a tuned tank circuit whose voltage level was monitored. The tank circuit was tuned by varying the voltage on a varactor. By applying a small 50-kHz modulation voltage to the varactor, an error signal was generated which could be detected and used to automatically tune the tank circuit. This feature eliminated any admixture of χ' due to mistuning, and greatly reduced microphonic noise.

For a maximum signal-to-noise ratio, the tank circuit must have a high Q, i.e., the length of the leads between the coil and the rest of the circuitry must be a minimum.[18] This was accomplished by placing a MOSFET (metal-oxide-semiconductor field-effect transistor) amplifier and the tuning circuitry *in situ*, housed in an active probe in the magnetic field. The Q of this circuit was about 110 at room temperature and 350 in liquid nitrogen. Outside the active probe, there was further rf amplification followed by simple diode detection. All further circuitry was dc coupled, eliminating the need for field modulation and giving a signal directly proportional to χ''. After detection, the tuning error signal was sent to a lock-in amplifier to provide feedback to the varactor, while the resonance signal was amplified by an instrumentation amplifier which used a stable reference voltage to null out the static dc level. The single-pass signal-to-noise ratio was about 10 for sodium and 3 for lithium. The output of the instrumentation amplifier was recorded by a Fabritek 1070 Instrument Computer, which digitized the signal into 512 channels and allowed signal averaging (usually 256 passes per "run"). The signal averager was interfaced with a PDP-8 minicomputer, allowing accumulated results to be punched on paper tapes and analyzed.

The magnetic field was supplied by a Varian V-3900 12-in. electromagnet with Fieldial regulation. An external sweep adaptor allowed the sweep to be controlled by a voltage from the signal averager,

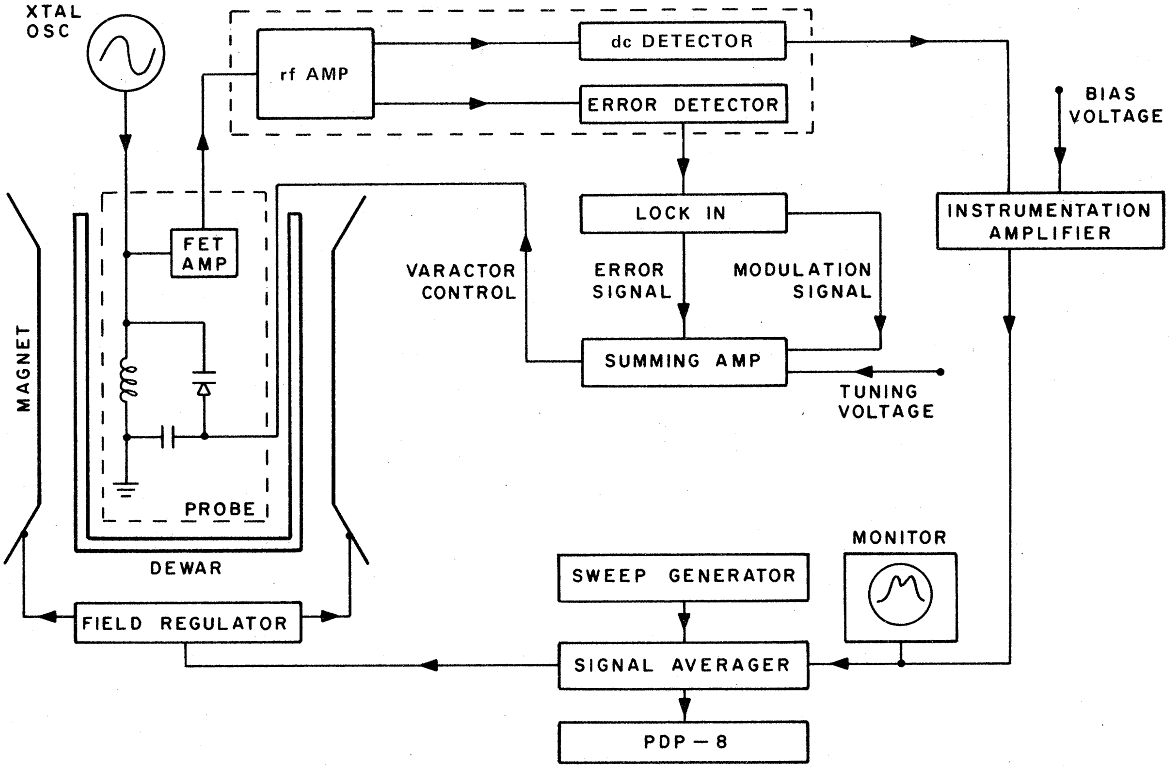

FIG. 1. Block diagram of the experimental apparatus.

and a zero field unit enabled the field to be swept through zero to −150 G. The field sweeps were accurately calibrated by fitting the ESR lines at low field or by using NMR channel markers at high fields.

The samples were in the form of dispersions of metallic particles in mineral oil. It was found that commercial preparations were much superior to home-made ones for this measurement. Apparently contamination introduced in the emulsification process made the final CESR linewidths independent of the purity of the initial bulk metal, so the signal to noise ratio was best for the commercial dispersions with their larger filling factors and better size homogeneity. A sodium dispersion supplied by MCB Corporation[19] had a 40% filling factor of 1-μ particles with a CESR T_2 of 4×10^{-8} sec at 77 K. A lithium dispersion was obtained from Lithcoa,[20] having 30% by weight metal with particles less than 10 μ and a T_2 of 10^{-7} sec at room temperature.

The data tapes generated in a run were analyzed by computer. Typical line shapes are shown in Figs. 2 and 3. The CESR lines were fitted to a Lorentzian by a linearized least squares program

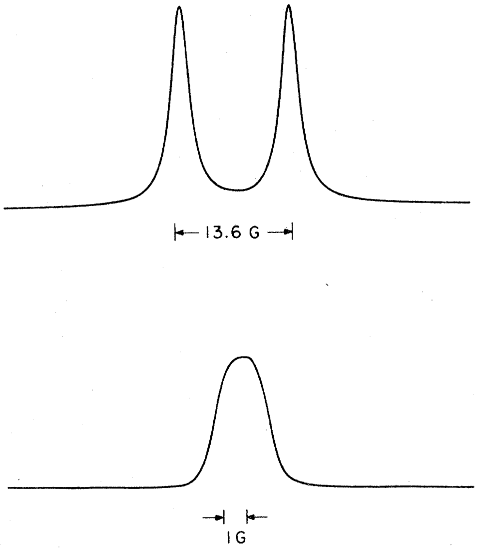

FIG. 2. Tracings of typical sodium CESR and NMR experimental lines at 77 K and 19 MHz. The experimental noise is less than the thickness of the traced line. The discrepancies between the experimental CESR line and a fit Lorentzian shape are also less than the thickness of the traced line.

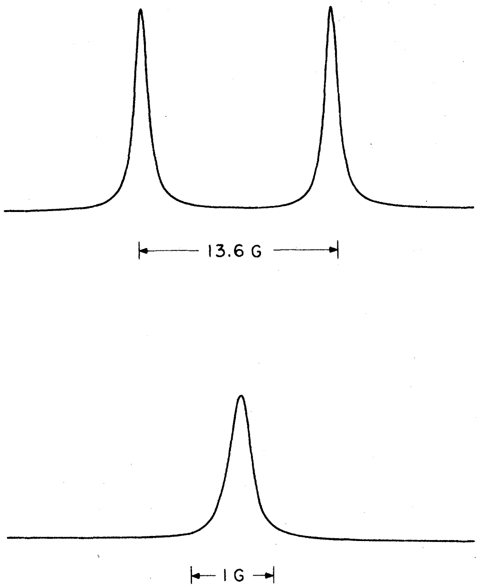

FIG. 3. Tracings of typical lithium CESR and NMR (Li^7) experimental lines at room temperature and 19 MHz. The experimental noise is less than the thickness of the traced line. Discrepancies between the experimental CESR line and a fit Lorentzian shape are comparable to the thickness of the traced line.

that handled over 400 points. The fit curves had excellent visual agreement with experimental ones, and the theoretical area ($\pi\times$amplitude$\times$ width) usually agreed with the measured area (with a wing correction) to about 0.1%. The NMR lines were of unknown shape but did not have broad wings; a baseline was determined from approximately 100 points sufficiently removed from the resonance, and the area above it was measured. The signal-to-noise ratios of the lines were judged to be between 100 and 200.

Although our measurement of the area under the NMR absorption line does not rely upon fitting an explicit function to the observed line shape, it is conceivable that some area might be lost in the wings from strain-induced quadrupolar "wipeout." We cannot entirely rule out the possibility of such effects, but we believe that they are unlikely to introduce significant errors. The alkali metals anneal readily, even at temperatures well below those of our measurements, so that impurities are probably the main source of lattice strains. Since we require high-purity specimens for other reasons, we expect that wipeout by impurities will also be small. Earlier measurements on sodium[8] by this method show no temperature dependence that cannot be accounted for by a change in the lattice constant, even when the specimen is taken through the well-known phase transformation.

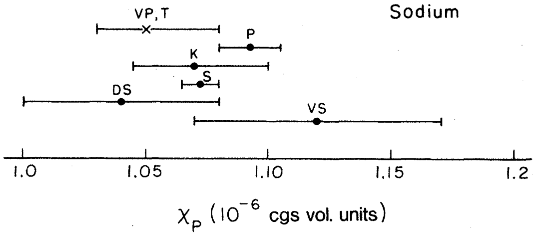

FIG. 4. Experimental and theoretical susceptibilities for sodium: VS-Vehse and Schumacher (Ref. 8); DS-Dunifer, Pinkel, and Schultz (Ref. 1); S-Perz and Shoenberg (Ref. 2); K-Kushida, Murphy, and Hanabusa (Ref. 9); P-present work; T-theory (Ref. 22); VP-Vosko, Perdew, and MacDonald (Ref. 23).

This method of analysis greatly reduced the likelihood of possible experimental errors. By fitting with a Lorentzian, all the area of the CESR curve is included. Studying the line shapes, the Lorentzian nature of the ESR and lack of wings in the NMR is confirmed. Distortions due to impurities, skin depth effects, admixture of χ', residual fields, or transients can be detected and corrected. By varying the rf field amplitude, it was found that the maximum saturation level was less than 0.2%. Thus the major source of error in the measurement is felt to be the experimental scatter of the data rather than any systematic uncertainties.

IV. RESULTS AND DISCUSSION

A total of 42 measurements were made on three samples of sodium at 77 K. These had a mean of 1.092 with a standard deviation of 0.009. (A factor of 10^{-6} and cgs volume units are understood for all values.) A total uncertainty of 0.012 reflects both the scatter in the data and the uncertainty in the experimental conditions—field sweep, saturation, temperature. Thirty-six measurements were made on three samples of lithium at 295 K, having a mean of 2.165 and a standard deviation of 0.037. The total uncertainty for Li is 0.039.

The results of recent measurements and calcula-

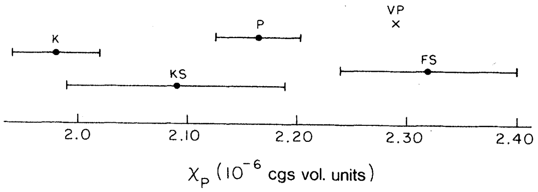

FIG. 5. Experimental and theoretical susceptibilites for lithium: KS-Kettler, Shanholtzer, and Vehse (Ref. 21); FS-Flesner and Schultz (Ref. 4); K-Kushida, Murphy, and Hanabusa (Ref. 9); P-present work; VP-Vosko, Perdew, and MacDonald (Ref. 23).

tions of the susceptibility are summarized in Figs. 4 and 5. Our results are in good agreement with those of Vehse and coworkers.[8,21] The experiments of Kushida[9] *et al.* were primarily concerned with the relative pressure dependence of the susceptibility rather than an absolute value and hence they did not account for the area in the electron wings. This systematic uncertainty may be responsible for the difference between their results and ours. Recent results for sodium by spin wave transmission techniques[1] and de Haas–van Alphen[2] measurements, both at liquid-helium temperatures, are shown. A spin-wave transmission measurement[4] recently yielded a value for lithium at liquid helium temperatures. It is seen that there is general agreement between our results and other experimental values.

The model that has received the most theoretical attention is "jellium," the homogeneous electron liquid. Because of its simple band structure, sodium should be fairly jellium-like, and the "consensus" value[22] of the predicted susceptibility is 1.05±0.03. Uncertainties in the effective mass, the lattice parameter, and the crystal structure (sodium undergoes a Martensitic transformation at 35 K) limit the use of the experimental results as a final test of the theory. Lithium has a more complex band structure and is treated very poorly by the jellium model. However, recent work by Vosko and coworkers[23] using the density-functional formalism has given results that agree with experiment at the 5% level for both sodium and lithium. This agreement shows the power of their approach, but to test their theory further it would be more beneficial to have experimental data from different metallic densities than to improve further the precision in metals already measured. In this respect, more information can be added by anchoring the values for the relative change from Kushida's measurements with the absolute values presented here to obtain information about the slope of the susceptibility curve versus density.

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