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The Paramagnetic Susceptibility of Lithium and Sodium Metal

NsG 533

Research Project NASA -11-63

Final Report

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FACILITY FORM 602

The original proposal for this grant consisted of the following projects:

(a) Remeasurement of the conduction electron susceptibility, χ_p^e, for lithium metal chiefly at room temperature. Some measurements at 77°K.

(b) Knight shift and susceptibility measurements in the same sample of sodium at 77°K.

(c) Relative susceptibility measurements in sodium as a function of sample preparation over the range 4°K to 77°K.

(d) Extension of technique to previously unmeasured substances.

(e) Effects of impurities on the susceptibility. Measurements will be made chiefly in sodium at 77°K with the possibility of some very low temperature measurements also.

These areas will be reviewed in detail.

I. Summary of Experiments

(a) Using a spin resonance technique first devised by Schumacher and Slichter[1], the paramagnetic susceptibility of the conduction electrons of metallic lithium was measured at room temperature. These results were reported in a paper at the "March 1966" meeting of the American Physical Society[2]. Copies of this paper are included with this report. It should be noted that the susceptibility has also been measured at 4.2°K. These results were also reported in part of the same paper. The measurements were in agreement with previous results. The low and high temperature results were essentially the same as predicted theoretically.

(b) Knight shift measurements were made in samples of sodium prepared by the same technique as was used for the susceptibility measurements. The purpose of this experiment was to provide clear cut evidence that existing calculations of the nature of the wave functions describing the electrons were incorrect. As expected no change in the Knight shift was observed as a result of sample preparation. The Knight shift measurements are reported in an unpublished masters thesis of Mr. Robert Jefferson[4].

(c) Low temperature (4.2°K) measurements of the absolute susceptibility of the conduction electrons in sodium have been made. These results are in good agreement with the 20°K and 77°K measurements of Schumacher and Vehse[5]. No relative measurements were made as it seems at present that absolute measurements are more convenient. The goal of these measurements is to determine whether or not a reported Knight shift anomaly might be due to a corresponding anomaly in the electron susceptibility[6]. Our precision is not yet high enough to rule out any susceptibility change.

These low temperature results will be reported in a meeting of the West Virginia Academy of Sciences in April 1966. An abstract of this paper is included with this report.

(d) We have tried to measure the susceptibility of metallic beryllium by the Schumacher-Slichter technique. Feher and Kip[7] have reported an electron resonance in beryllium and give an approximate value for χ_p^e. We have searched under conditions such that we should have been able to measure the susceptibility, but have not been able to observe the resonance. Other investigators have not been successful in reproducing the results of Fehere and Kip. The work on this part of the project has been discontinued.

(d & e) The effect of impurities on the susceptibility has been investigated in metallic lithium. We have made some alloys of traces of magnesium and lithium. There is an apparent decrease in the susceptibility upon alloying but the research has not yet progressed to the point where we wish to publish our findings. The work is being continued. A report will be submitted to NASA upon completion.

II. Evaluation of Results

It is felt that our research has made two definite contributions to scientific knowledge. We have cleared up any existing doubts as to the accuracy of previously reported measurements of the conduction electron susceptibility of lithium. We have made better absolute measurements of this quantity in metallic sodium than have previously been made. Our results on the Li-Mg alloys should be of definite interest to those studying the properties of metals.

III. Publication Plans

Already Published

W. L. Shanholtzer and W. E. Vehse, Measurement of the Electron Spin Susceptibility of Metallic Lithium
Bull. Am. Phys. Soc. <u>Ser. 11 Vol. 11</u>, 220, 1966.

Planned Publication

R. L. Stenger and W. E. Vehse, Conduction Electron Susceptibility of Metallic Sodium at $4.2^{\circ}K$. To be presented at the W.Va. Academy of Sciences April 1966.

Upon completion of this phase of the work, a review of all measurements to date will be submitted for publication.

J. E. Kettler and W. E. Vehse, Conduction Electron Susceptibility of Li-Mg Alloys (to be presented for publication upon completion of the work)

IV. Continuation of this Research

A proposal has been submitted to the AEC for funds to continue this project. The reviews have been favorable. The proposal is being held for consideration when the budget for the next fiscal year is available.

V. Expenditures.

Salaries,

Principle Investigator		$1200.00
½ Assistant		4888.88
Workmen's Comp. TIAA, Soc. Sec.		30.88
	TOTAL	$6119.76
Capital Equipment.		
Centrifuge		160.50
Frequency Meter		79.50
VTVM		63.55
Heat Gun		38.83
Large Vacuum Pump		760.35
Audio Oscillator		332.90
Power Supply		281.95
Vacuum Pump		147.29
Isolator Lab		615.00
Dewar Assembly		230.00
Isotemp Oven		436.00
Ultrasonic Probe		890.00
	TOTAL	$4035.87
Coolants		
Nitrogen		65.00
Helium - (including rentals)		265.00
	TOTAL	$ 330.00
Miscellaneous		
Hardware		
Electronic Parts		
Chemicals		
Film		
	TOTAL	$1217.76
	Total Expenditures -	$11703.39

Total Allocated	$11,809.00
Expenditures	11,703.39
Unused Balance	$ 105.61

Note: Some invoices are as yet outstanding so that the above figures based on a few estimates may change by a few dollars. A corrected tabulation of expenditures will be forwarded as soon as possible.

FOOTNOTES

1. R. T. Schumacher and C. P. Slichter, Phys. Rev. 101, 58 (1956).

2. W. L. Shanholtzer and W. E. Vehse, Bull. Am. Phys. Soc. Ser 11 Vol. 11, 220 (1966)

4. G. R. Jefferson, Thesis (unpublished) West Virginia University.

5. R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids, 24, 297, (1963).

6. D. W. Feldman and W. D. Knight, Private Communication to R. T. Schumacher.

7. G. Feher and A. F. Kip, Phys. Rev. 98, 337, (1955).

THE ELECTRON SPIN SUSCEPTIBILITY OF METALLIC LITHIUM

W.L. Shanholtzer and W.E. Vehse
West Virginia University

I. INTRODUCTION AND MOTIVATION FOR PRESENT RESEARCH

The static magnetic susceptibility of a metal is usually slightly paramagnetic. This is due to the paramagnetism of the conduction electron spin moments. The contribution of the spin moments to the total susceptibility may be isolated and measured for certain metals, including lithium, using a spin resonance technique first devised by Schumacher and Slichter[1].

The motivation for the present research was to increase the precision of the original room temperature measurements of Schumacher and Slichter, which, because of the work of Schumacher and Vehse[2], we felt might be in error by as much as twenty percent. In addition, we wished to extend the measurement to liquid helium temperatures, which we have recently completed. We proposed to increase the precision by a more systematic analysis of the integrated area under the electron spin resonance absorption curve from which the paramagnetic susceptibility is determined.

II. TECHNIQUE

The technique that we use in the measurement involves the observation of the radio-frequency spin susceptibility for both the nuclei and the conduction electrons. The measurement is made in the same sample at constant frequency, changing only the applied magnetic field.

It is possible to show[3] that the paramagnetic susceptibility of either nuclei or electrons is related to the integrated area under the resonance absorption curve plotted as a function of the magnetic field, i.e.;

$$\chi_p = \frac{2\gamma}{\pi\omega}\int_0^\infty \chi''(H_0)\,dH_0 ,$$

where γ is the nuclear or electronic gyromagnetic ratio, ω the frequency of the applied rf field, and $\chi''(H_0)$ the absorption component of the complex magnetic susceptibility. If we designate the integrals by A_e for the integrated area under the electron resonance curve and by A_n for the area under the nuclear resonance curve, we see that for a given freouency we have:

$$\chi_p^e = \chi_p^n \left(\frac{\gamma_e}{\gamma_n}\right)\left(\frac{A_e}{A_n}\right),$$

which is our working equation. The constants γ_e and γ_n are known and the nuclear susceptibility is given accurately by the Langevin-Debye formula:

$$\chi_p^n = N_n \gamma_n^2 \hbar^2 I(I+1)/3kT$$

where N_n is the number of nuclei/unit volume, I the nuclear spin, and $\hbar$,k,T all have their usual meaning. Thus the experiment consists of a simple comparison of areas.

The measurements were performed at ordinary radio frequencies. Q-meter detection is employed. The experimental apparatus is described in reference 2.

The samples were paraffin oil or paraffin wax dispersions of lithium particles.

Pictures of the electron and nuclear resonances are taken with a Polaroid camera; projected and traced on graph paper. A base line for the curves is determined and the experimental integration performed by counting squares. As we mentioned earlier, a new feature of our work is a more detailed analysis of the integrated area under an electron spin resonance absorption curve. Because the electron spin resonance curves have broad Lorentzian tails, some portion of the total area may be excluded when drawing in the experimental base line. In our analysis of the area we compute the fractional error in the experimental integration due to the displacement of the base line from its true value and correct the measured area accordingly. Corrections of from 5 - 20% consistently yield the same values of χ_ρ^e giving us additional confidence in our correction procedure. Determination of a base line for the nuclear resonance curves is no problem for the low temperature measurements, since the curves, which appear to be Gaussian, fall off very rapidly in the wings. (There is some question about the room temperature measurements as to whether it might be desirable to apply a small correction to the nuclear resonance areas also.)

III. RESULTS OF THIS MEASUREMENT

The results that we report for the conduction electron spin susceptibility of metallic lithium are:

at 300°K. .... $2.09 \pm .06 \times 10^{-6}$ cgs volume units.

at 4.2°K. .... $2.18 \pm .20 \times 10^{-6}$ cgs volume units.

IV. COMPARISON WITH OTHER VALUES

Comparison of Experimental and Theoretical Values of χ_ρ^e

Experimental:

Schumacher and Slichter[1]	$2.08 \pm 0.1 \times 10^{-6}$
Hecht[4]	$1.96 \pm 0.1 \times 10^{-6}$

Theoretical:

Pines [5]	1.90×10^{-6}
Shimizu[6]	2.12×10^{-6}
Silverstein[7]	2.20×10^{-6} ($0^{o}K$)

In addition to the above direct comparisons, one can obtain χ_p^e from related measurements. The Knight shift of the nuclear resonance is related to χ_p^e through the equation

$$K = B \chi_p^e \frac{P_F}{P_A}$$

where K is the Knight shift.

B is a collection of well known constants

P_F is the electron probability density at the nucleus averaged over the Fermi surface and

P_A is similar to P_F except that the average is for the free atom.

The Overhouser or "day" shift, D, is given by a similar expression.

$$D = B' \chi_p^n \frac{P_F}{P_A}$$

Combining these one has,

$$\chi_p^e = \frac{K}{D} \frac{B}{B'} \chi_p^n$$

Using the published values of K and D, one can infer that

$\chi_p^e = (1.90 - 1.98) \times 10^{-6}$ cgs vol. units.

The Korringa relation given in modified form by Pines[5] relates χ_p^e to the nuclear spin lattice relaxation time, Tie; the absolute temperature, T; the Knight shift, K; the ratio of the specific heat constant for a real metal to that of the free electron model, C/C_{free}; and the conduction electron susceptibility of the free electron model, $\chi_p^e/\chi_{p\,free}^e$. This relation is

$$T_{1e} T K^2 = \frac{\hbar}{4\pi k}\left[\frac{\gamma_e}{\gamma_n}\right]^2\left[\frac{C_{free}}{C}\right]^2\left[\frac{\chi_p^e}{\chi_{p\,free}^e}\right]^2$$

One obtains a χ_p^e of 2.3 X 10^{-6} cgs vol. units using the best current values for the experimental quantities.

V. CONCLUSION

We conclude that the measurements of χ_p^e as originally reported by Schumacher and Slichter are essentially correct and in agreement with our low temperature measurements.

VI. ACKNOWLEDGEMENTS

The support of NASA is gratefully acknowledged. We also wish to thank Mr. R. L. Stenger for the use of his equipment in performing our low temperature measurements.

FOOTNOTES

1. R. T. Schumacher and C. P. Slichter, Phys. Rev. 101, 58, (1956).

2. R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids, 24, 297, (1963).

3. R. T. Schumacher, T. R. Carver, and C. P. Slichter, Phys. Rev. 95, 1089 (L) (1954).

4. R. Hecht, Phys. Rev. 132, 966, (1963).

5. D. Pines, Solid State Physics (Academic Press, Inc., New York, (1956), ed. F. Seitz and D. Turnbull, Vol. I, p. 367.

6. M. Shimizu, J. Phys. Soc. Japan, 15, 2227, (1960).

7. S. Silverstein, Phys. Rev. 130, No. 5, 1703, (June 1963).

Conduction Electron Susceptibility of Metallic Sodium at 4°K.

by R.L. Stenger Jr. and W.E. Vehse

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ABSTRACT

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Using a spin resonance technique, the paramagnetic contribution of the conduction electrons to the total susceptibility of metallic sodium has been isolated and measured at 4°K. A Robinson NMR spectrometer was used to make these measurements. The results are in excellent agreement with measurements at 20°K and 77°K. The precision is not yet high enough to rule out a change in the susceptibility as the cause cf a Knight shift anomaly at low temperatures however.