the germanium-electrolyte interface near the small-angle grain boundary is therefore reduced and the etching consequently retarded.

The dislocations in such boundaries are commonly of the order of 10^{-4} cm apart. Etching studies[1] show that dislocations of a different character are scattered throughout the crystal with a similar (3-micron) inter-dislocation spacing. The above observation shows, therefore, that not all the dislocations are equally effective as recombination centers. Such observations do not show whether the dislocations are themselves the recombination centers or merely the preferred sites for impurity atoms which behave as recombination centers.

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Magnetic Susceptibility of Sodium Metal

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The total susceptibility of sodium metal has been measured from room temperature down to 55°K using the Gouy technique. The mass susceptibility at room temperature was found to be $+(0.70\pm0.03)\times10^{-6}$ cgs units. This result is analyzed by using an estimate of the ion core susceptibility and calculations of the conduction-electron spin contribution. The analysis leads to a conduction-electron orbital diamagnetism which is much smaller than the value obtained from the Landau-Peierls formula. No explanation is given of this disparity.

The susceptibility decreases by 4.5% between room temperature and 55°K. No abnormal behavior was found in the susceptibility between 77°K and 55°K where the Knight shift exhibits an anomaly. An account is given of experimental difficulties which were encountered in an attempt to measure the susceptibility at liquid helium temperatures.

INTRODUCTION

THE total magnetic susceptibility χ of metallic sodium is the sum of three components, namely, the diamagnetism of the core electrons χ_c, the paramagnetism due to the spin of the conduction electrons[1] χ_s, and the diamagnetism due to the orbital motion of the conduction electrons[2] χ_0. In this paper we shall be interested in the magnitude of these components.

For simple metals such as sodium, the contribution due to the core can be determined indirectly from the measured susceptibility of sodium salts[3] and can also be calculated with reasonable confidence using Hartree-Fock wave functions.[4] The determination of the two conduction-electron contributions, particularly the orbital component, is much more difficult. The free-electron calculations, while giving a qualitative understanding of why the susceptibility is almost temperature-independent, are not satisfactory quantitatively. The susceptibility of sodium computed on the basis of the free-electron model[5] leads to a value which is too low by a factor of 3.

A number of recent developments have renewed interest in the susceptibility of sodium metal, particularly concerning the determination of the component susceptibilities. First, an experimental technique has been developed for measuring the spin contribution directly.[6] Only lithium has been studied so far but measurements on sodium are being made currently. Secondly, new theoretical values have been published for the spin contribution. Pines[7] has applied the Bohm and Pines collective-electron theory to this problem. Furthermore, calculations have been made by Townes, Herring and Knight[8] and by Kohn and Kjeldaas[9] of the spin contribution from the experimental value of the Knight shift in sodium.

With the value of ion core susceptibility and these recent values for the spin contribution, an estimate of the orbital contribution can be obtained if the total static susceptibility is known. Since there is a wide scatter in the published data,[10] we have redetermined this total susceptibility.

Apart from the absolute value of the susceptibility at room temperature, we have measured the suscepti-

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TABLE I. Details of four specimens and values of the susceptibility obtained with each of them.

Dimensions of sodium		Magnetic force due to Na	Mass susceptibility
Area (cm^2)	Length cm	Magnetic force due to quartz	of Na (cgs units)
0.138	7.6	1.70	0.687×10^{-6}
0.138	7.6	1.80	0.720×10^{-6}
0.108	7.6	1.55	0.708×10^{-6}
0.107	5.4	1.55	0.702×10^{-6}

bility as a function of temperature down to 55°K. In the free-electron picture of the conduction-electron susceptibility, there should be no change apart from the effects of thermal expansion on the Fermi energy. Changes with temperature might occur, however, due to electron-phonon interaction at low temperatures.[11] It is to be noted that Knight[12] has found an anomaly in the Knight shift in sodium below 77°K; if this anomaly is connected with a density of states change, it should be seen in the susceptibility.

METHOD

The measurements of susceptibility have been made using the Gouy technique. A Gulbransen-type microbalance[13] has been used to measure the force on the specimen; the balance is capable of measuring a force of 1 μg with a 3-g load. Due to its great sensitivity, only moderate magnetic fields, less than 4000 gauss, are required for the measurement of susceptibility.

The sodium used for the specimens was supplied by the Ethyl Corporation. According to chemical analysis there was no strongly paramagnetic or ferromagnetic impurity present in concentrations greater than 0.0002%. (The absence of ferromagnetic impurities was demonstrated also by the fact that we found the susceptibility to be independent of the magnetic field. The small change in the susceptibility with temperature found in this work indicates the low level of paramagnetic impurities.) Potassium appeared to be the most abundant impurity, and chemical analysis showed it to be less than 0.01%.

In order to make a specimen from the metal, the oxide was first removed from the sodium under pure benzene. It was placed in a quartz tube and the benzene pumped off. The sodium was then melted under high vacuum. On melting, the sodium breaks any remaining oxide coat; the oxide coat sticks to the wall of the quartz tube and it is very easy to remove the shiny metal from inside. The sodium was allowed to flow out of the oxide and was pushed into a thin-walled quartz tube, the final containing tube, by the pressure of pure helium gas. This quartz tube was sealed off just above the sodium level so as to include some helium gas for thermal exchange. Using this technique we were able to cast cylinders of sodium about 7 cm long and $3\frac{1}{2}$ mm diameter in quartz tubes of various wall thickness ranging between $\frac{1}{2}$ and $\frac{1}{3}$ mm. The cylinders of sodium produced in this way had very little cavitation and there was no visible oxide. Quartz has been used as a container because its susceptibility has been found to be almost temperature independent, and in addition it has been suggested that sodium reacts slightly with Pyrex, especially at high temperatures, producing free radicals which are paramagnetic.

The quartz tube makes a substantial contribution to the observed force on the specimen (see Table I) so its contribution must be accurately determined. This has been done in two ways. First, the susceptibility of quartz glass has been measured between room temperature and 1.5°K and the container contribution calculated from this and the measured dimensions of the container. Secondly, pieces of quartz which were ultimately to be used for containers were measured independently. The values of the quartz contribution obtained by the two methods were in agreement to 5%. A further check on the accuracy of the correction has been obtained by varying the dimensions of the specimen so as to change the quartz contribution relative to that of the sodium (Table I). No consequent systematic error appeared in the final value for sodium. We are restricted to these methods of determining the quartz contribution since we wished to preserve the final specimens.

The sensitivity of the balance used to measure the magnetic force has been determined using small calibrated weights and also by bouyancy measurements on a specimen of known volume. The magnetic field was measured with a fluxmeter which has been calibrated by proton resonance. In order to check this absolute calibration of the apparatus, we have measured the susceptibilities of: (1) triply distilled water which had been passed through an ion exchange column and boiled to remove air; (2) zinc sulfide with 0.1% manganese incorporated, and (3) oxygen gas. These three calibrations together with the absolute calibration show a scatter of 6%. The calibration used for the final data reduction was the mean of these. Considering the large correction for the quartz container and the scatter of the calibration data, we believe the final data given for the susceptibility at room temperature is accurate to 5%. The relative change in the susceptibility with temperature is accurate to 1%.

The data for the susceptibility below room temperature has been corrected for thermal contraction assuming that the quartz container does not restrain the decrease in cross section of the sodium. (The variation of the magnetic force with temperature, the experimentally determined quantity, is proportional to the product of the susceptibility per unit mass, the density, and the area of cross section of the specimen. If the

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container with its negligible contraction had kept the area constant, allowing the sodium to contract in length only, the sole correction would be through the density change, where as our data allows for both density and area changes.) The container may effect the contraction slightly, hence there is some uncertainty in the correction made.

RESULTS

The values obtained for the susceptibility at room temperature are given in Table I. The average value for the mass susceptibility of the four specimens at room temperature is 0.70×10^{-6} cgs units. The variation with temperature down to 55°K is shown in Fig. 1 in the form of the percentage change from the room temperature value. The susceptibility decreases by 4.5% between room temperature and 55°K.

It was originally intended to measure the susceptibility from 300°K to 1.5°K. However, experimental difficulties prevented work in the liquid helium range.

The principal difficulty is due to electromagnetic damping of the specimen in the magnetic field, the damping being proportional to the conductivity of the specimen. At room temperature this is not serious, but because of the purity of the sodium, its electrical resistance may fall by a factor of 1000 between room temperature and 4°K,[14] and the balance becomes seriously over-damped. It is easily calculated that one would have to wait several hours for equilibrium at 4°K for the specimens which we have used. Observation of the damping of the balance at higher temperatures leads us to estimate that 30°K to 40°K would be the lowest temperatures at which measurements could have been made.

One way of overcoming this difficulty is to cut up the specimen and "laminate" it in some way. We have not found a satisfactory way of doing this for sodium (although it is quite easy for metals such as copper) because one wishes to avoid the presence of insulation materials which may react with the sodium, and also because one would have to study carefully the magnetic properties of the insulation. We have also considered the possibility of introducing trace impurities to reduce the conductivity but this would lead to uncertainties in the evaluation of the susceptibility data. There is very little one can do with the balance system, leaving the specimen unchanged, to reduce the damping. A lower sensitivity balance would have a smaller damping time, but the accuracy of measuring the magnetic force would also be smaller. Similarly, reducing the magnetic field reduces the damping but the magnetic force is reduced in the same proportion.

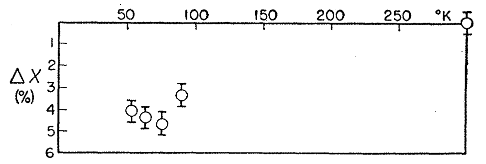

FIG. 1. The variation of the susceptibility of sodium with temperature.

TABLE II. Theoretical estimates of the mass susceptibility of sodium,[a] in cgs units.

	I	II
χ_c	-0.23×10^{-6}	-0.23×10^{-6}
χ_s	$+0.68\times10^{-6}$	$+0.86\times10^{-6}$
χ_0	-0.23×10^{-6}	-0.23×10^{-6}
Total χ	$+0.22\times10^{-6}$	$+0.40\times10^{-6}$

[a] Experimental total $\chi=+0.70\times10^{-6}$.

We have observed another effect which renders work at the lower temperatures difficult. Between 77°K and 4.2°K, the sodium ruptured the quartz container of the two specimens which were used. This phenomenon has not been examined in detail but it might be connected with the phase transformation in sodium observed by Barrett[15] in this temperature range. It seems unlikely that the normal difference in thermal contractions could be the cause because the bulk of the volume changes occur between room temperature and 77°K and it is quite certain that the rupture did not occur in this range.

DISCUSSION

We shall first discuss the value of the susceptibility at room temperature. The value we obtain is slightly higher than the two most recent previous determinations of the susceptibility[10]; it is 6% higher than the value due to Klemm and Hauschulz, and 7% higher than that due to Lane and Bieler. Our value is at least 17% higher than that found in any work previous to these authors.

In Table II we have constructed two theoretical values which may be compared with our experimental value. Column I uses the free electron value for the spin contribution while Column II uses the value due to Pines and Kohn and Kjeldaas. The value for the core susceptibility is a mean value derived from measurements on sodium salts and also direct calculations from the electronic wave functions. The orbital contribution used in both columns is the Landau-Peierls free electron value. It can be seen that there is a serious disparity between these calculated values and the experimental value. Indeed no experimental value for sodium has been reported in the literature as low as these calculated values.

It seems unlikely that the disparity can be due to the value for the ion core. The observed susceptibility of neon, which has the Na^+ configuration, suggests that it is unlikely to be in error by more than 20%. With regard to the spin contribution, Kohn and Kjeldaas

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[15] C. S. Barrett (private communication).

claim a 5% accuracy for their calculation while Pines claims 20% for his. Unfortunately, we do not have as yet an independent experimental value for this spin contribution. However, these two different types of calculation do give the same result, and in the case of lithium, for which χ_s has been measured, the calculations are in good agreement with the experimental value.

Thus we conclude, that if the value of the orbital contribution is that given by the Landau-Peierls formula, the susceptibility of sodium is anomalously high.

If either of the values for $\chi_s+\chi_c$ in Table II are accepted as correct, then our experimental value is seen to imply a surprisingly small value for the orbital diamagnetism. Using the free electron χ_s, we obtain $\chi_0=+(0.25\times10^{-6})$; using the Kohn and Kjeldaas value, we obtain $\chi_0=+(0.07\times10^{-6})$. The value of $-(0.23\times10^{-6})$, expected on the free-electron theory, differs from both of these by several times the estimated error.

We have no explanation of these disparities. While it is true that according to the band theory of metals, the Landau-Peierls formula does not give the complete orbital susceptibility,[16] it would be surprising if the correction terms were responsible.

Finally, we shall discuss the low-temperature data. The decrease in susceptibility by 4.5% from room temperature to 55°K is roughly what is to be expected from the change in the Fermi level with density. Below 77°K, we have found no sign of an anomaly similar to that found in the Knight shift in sodium[12] which changes by 5% between 77°K to 55°K. Thus we conclude that, at least in the limited temperature range 77°K to 55°K, the behavior of the Knight shift is not due to a rapid change in the density of states.

Note added in proof.—After submitting this paper, we received a preprint of a paper by Schumacher and Slichter which gives the results of their measurement of the conduction electron spin susceptibility in sodium. (This paper is to appear soon in *The Physical Review.*) They obtain for χ_s a value per g of $(0.96\pm0.1)\times10^{-6}$ cgs units corrected to room temperature. If one uses the value of 0.96×10^{-6} to calculate the orbital diamagnetism as described in the discussion above, one obtains $\chi_0=-0.03\times10^{-6}$. This is still much less than the free electron value of -0.23×10^{-6}. However, the uncertainties in the values of χ_s, χ_c and the total χ are now such that a combination of extreme values of these quantities can lead to a χ_0 close to the free electron value. Hence, the existence of a substantial deviation of the actual orbital diamagnetism from the free electron value, while appearing most likely from the data, is not definitely established.

ACKNOWLEDGMENTS

We wish to acknowledge the helpful discussions we have had with E. N. Adams, T. Kjeldaas, and W. Kohn.

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Electroluminescence of GaP

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Electroluminescence has been observed in GaP single crystals. Above a threshold current the intensity of the emitted light is proportional to the ac and dc passing through the crystals. The orange color of the light emission probably is due to the presence of Ga as activator, while the brilliant, deep red luminescence is observed in crystals where Zn is a possible activator. The temperature dependence of the luminescence is negligible in the range from liquid nitrogen temperature to 160°C. The impact excitation mechanism of Piper and Williams is proposed.

SINGLE crystals of GaP have been prepared[1] which were found to emit orange-colored light when either dc, or ac (up to 20 000 cps) is applied. Massive In, Ga, Hg, Cd, Zn, Pb, conducting glass, and point contacts of W were used as electrodes. Above a threshold current, the light intensity is proportional to the ac and dc passing through the crystals (Fig. 1), as has been found for SiC [2] and ZnS:Cu [3]; it increases exponentially with voltage. Since rectification is found in the crystals, the light output in the forward direction is less than in the reverse direction. This also holds true when ac is applied; the light pulses observed are in phase with the applied voltage and are sinusoidal. This was determined with an oscilloscope by synchronizing the photomultiplier (RCA 5819) output with the voltage applied (Fig. 2). There were no out-of-phase pulses observed. The decay time, as derived from the ac measurements, is less than 25 μsec. Using dc, the light emitted from the majority of the crystals appears in the vicinity of the

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