field dependence became significant especially in the intermediate temperature range as is shown for sample As[11] in Fig. 8.

For the *p*-type sample discussed in the preceding section, Fig. 9 gives the results of similar measurements. Particularly noteworthy is the shift of the Hall crossover (sign change) to higher temperatures with increasing field strengths. The direction of this shift is that qualitatively predicted by a strong-field, isotropic theory treatment such as given by Madelung.[14] Willardson, Harmon, and Beer[15] point out that though InSb has a similar shift, the shift observed in germanium is in the opposite direction. To explain this fact they introduce the concept of "fast holes," showing that the results can be explained by assuming a mixture of ordinary and high mobility holes taking part in the conduction process. At present, such a model seems unnecessary for gray tin.

[14] O. Madelung, Z. Naturforsh. **8a**, 791 (1953).
[15] Willardson, Harmon, and Beer, Phys. Rev. **96**, 1512 (1954).

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Magnetic Susceptibility of Copper Metal at Low Temperatures

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The total magnetic susceptibility of high-purity copper has been measured between 300°K and 1.45°K using the Gouy method. It is found that the mass susceptibility can be represented by $\chi=(-0.083+0.023/T)\times10^{-6}$ cgs unit. This temperature dependence is much smaller than that found by previous workers, whose data extends only down to 14°K. An anomaly in the susceptibility at low temperatures, previously reported, was not found. The nuclear susceptibility of copper is responsible for about one-fifth of the temperature dependence found in the present work; the remainder can be explained by a paramagnetic impurity content which is plausible for the particular copper used. It is concluded that the susceptibility of pure copper is substantially independent of temperature in the measured range.

I. INTRODUCTION

THERE have been reported in the literature two measurements of the temperature dependence of the magnetic susceptibility of copper between room temperature and 14°K.[1,2] No measurements at lower temperatures have been published.[3] The two measurements down to 14°K are in substantial disagreement with each other. According to de Haas and van Alphen,[1] the magnitude of the susceptibility of copper increases monotonically with decreasing temperature, the value at 14°K being 12% higher than at room temperature. On the other hand, Bitter *et al.*[2] found that the susceptibility first increases about 3% as the temperature is reduced from 300°K to 63°K, but subsequently gets rapidly smaller, decreasing by 35% between 63°K and 14°K.

Either of these results, if correct, would be difficult to understand because one would expect the magnetic susceptibility to be substantially independent of temperature. Using a free-electron picture, the only temperature dependence expected would be due to the effect of changes in bulk density on the Fermi level and the total effect of this would be less than 2%. Most of this change would be concentrated at the higher temperatures. Even a theory which takes into account the energy band structure of copper does not suggest a temperature-dependent susceptibility. A more refined model of a metal can, however, lead to a temperature-dependent susceptibility at very low temperatures, if the density of states is affected by a temperature-dependent electron-phonon interaction.[4] Anomalies in the magnetic susceptibility of copper would be of particular interest inasmuch as the noble metals are considered to have a relatively simple electronic structure.[5]

In the experiments to be described in this paper, the magnetic susceptibility of very pure copper has been

[1] W. J. de Haas and P. M. van Alphen, Leiden Comm. 225b (1933).
[2] Bitter, Kaufmann, Starr, and Pan, Phys. Rev. **60**, 134 (1941).
[3] Some indication of the behavior of the susceptibility in the liquid helium range can be obtained from experiments by L. Mackinnon [Ph.D. thesis, Cambridge University, 1949 (unpublished)]. His results suggest that the susceptibility decreases by about 5% between 4.2°K and 1.4°K. Because of experimental difficulties, this result is not well established.
[4] M. J. Buckingham, Nature, **168**, 281 (1951); M. J. Buckingham and M. R. Shafroth, Proc. Phys. Soc. (London) **A67**, 828 (1954).
[5] H. M. Krutter, Phys. Rev. **48**, 664 (1935); D. J. Howarth, Proc. Roy. Soc. (London) **A220**, 513 (1953).

measured between 300°K and 1.45°K. We wished to resolve the discrepancies between the earlier measurements and also extend our knowledge of the susceptibility into the liquid helium range. (There have been no previous total static susceptibility measurements made of any of the highly conducting simpler metals in the liquid helium range of temperatures.) A technical difficulty arising in measurements at low temperatures,[6] due to induction damping of the motion of the specimen in the magnetic field, has been overcome.

II. METHOD

The susceptibility measurements have been made using the Gouy technique, the apparatus being identical to that used in previous work on sodium.[6]

The copper used for the specimen was the highest purity copper known to be available. This is supplied by the American Smelting and Refining Company and is quoted as 99.999% copper. In a study of this high-purity copper, Smart *et al.*[7] were not able to detect any impurity by spectrographic analysis. For our experiments, freedom from strongly paramagnetic and ferromagnetic impurity is most important. In this class of impurity, iron and nickel are the two most likely to be found and it is estimated by Smart *et al.* that the concentration of each of these in the copper is less than a part per million. The bulk metal has a residual electrical resistance ratio of approximately 1/1000, which is a factor 3 lower than that of any other high-purity copper available commercially.[8]

In order to avoid difficulties due to electromagnetic damping, the specimen shown in Fig. 1 was used. It consisted of 50 wires of 0.3 mm diameter spaced apart from each other by two disks of Teflon. Great care was taken to avoid contamination in drawing the wire down from the bulk metal. The wire was frequently etched to remove surface contamination, especially before annealing. A piece of the final annealed wire was clamped between two terminals for a residual resistance measurement *without annealing after the handling and clamping*. The residual resistance value was found to be 1/350 which indicates that very little impurity could have entered during the wire-drawing process.[9]

The specimen shown in Fig. 1 was made from cleaned and annealed wire but after the specimen had been constructed, the whole specimen was cleaned and reannealed.

The procedure used for calibrating the balance has been described earlier.[6] The correction for the Teflon end pieces was 3% at all temperatures. The correction which allows for thermal contraction of the specimen

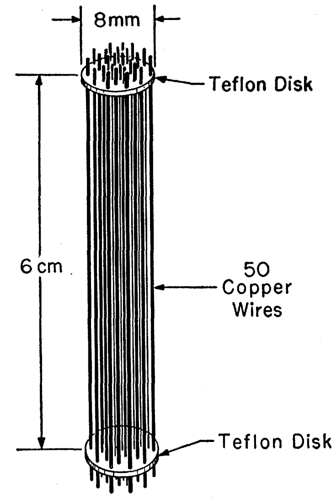

FIG. 1. Diagram of specimen.

below room temperature is only a fraction of a percent and has been neglected.

Previous work with a dilute magnetic salt (ZnS; 0.1% Mn) has demonstrated that there is temperature equilibrium between the specimen and surrounding low-temperature bath.[6] Hence we have determined the temperature of the copper specimen from measurements of the vapor pressure of the surrounding refrigerant. This method is, however, subject to doubt when the refrigerant is entirely in the solid phase. One of the measurements of the susceptibility of copper has been made using solid hydrogen and the temperature of this determination will be specified in the table of results as 10±1°K. Past experience in the use of solid hydrogen suggests that the actual temperature is within the limits specified.

III. RESULTS

The susceptibility was found to be independent of magnetic field between 1500 gauss and 4400 gauss. Below 1500 gauss, the susceptibility was found to be slightly field dependent at all temperatures. We presumed that this was due to ferromagnetic inclusions in the specimen which are saturated by external fields greater than 1500 gauss. The concentration of ferromagnetic impurity is too small to be observed when saturated. The susceptibility data recorded below are the field independent values.

The values obtained for the susceptibility per unit mass at various temperatures from 300°K to 1.45°K are listed in Table I. The period of the balance observed at the lowest temperatures indicated that the damping was well below the critical value.

The susceptibility is plotted against $1/T$ in Fig. 2. The relation

$$\chi=\left(-0.083+\frac{0.023}{T}\right)\times10^{-6}$$

represents the data with a mean scatter of 1%.

[6] R. Bowers, Phys. Rev. **100**, 1141 (1955).
[7] Smart, Smith, and Phillips, Am. Inst. Mining Met. Engrs. **143**, 272 (1941).
[8] M. Garfunkel (private communication).
[9] The drawing procedure which enabled us to maintain the purity of the copper was devised by Dr. J. C. R. Kelly, whose important contribution is gratefully acknowledged.

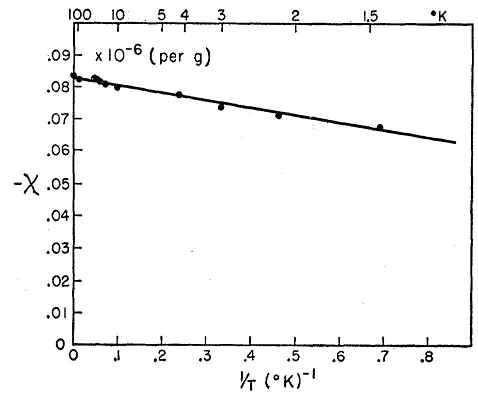

FIG. 2. The magnetic susceptibility of copper.

IV. DISCUSSION

The value we obtain for the susceptibility of copper at room temperature is 1.5% lower than the value obtained by Bitter *et al.* It is 3.5% lower than a mean value of various previous determinations.[10]

The temperature dependence observed by us does not agree with that found in either of the two previous determinations. From 300°K to 14°K we find only a small change in the diamagnetic susceptibility; it decreases by 3.5%. De Haas and van Alphen found an increase of 12% in this range while Bitter *et al.* found an increase of 3% between 300°K and 63°K, followed by a decrease of 35% between 63°K and 14°K. Our data below 14°K, also, shows no sign of the latter anomaly. The change in the susceptibility which we find on the liquid helium range is somewhat larger than that suggested by Mackinnon's work (see reference 3).

In any evaluation of the work described above, consideration must be given to two important experimental features. Clearly, the copper must be very pure, particularly free of paramagnetic and ferromagnetic impurities. No analysis is given of the specimens used by de Haas and van Alphen but they say that no ferromagnetic impurity was present. The sign of their temperature dependence is in any case opposite to that one would expect from paramagnetic impurities. The copper used by Bitter *et al.* was the same A.S.R. high-purity copper used in our work; it had less than 0.00007% iron in it, and the anomaly observed by them does not appear to be explainable in terms of paramagnetic impurities. The second point concerns a difficulty arising in the measurement of very pure specimens. When one uses a magnetic balance, electromagnetic damping of the specimen in the magnetic field can become very troublesome at low temperatures.[6] De Haas and van Alphen had difficulty with this and as a result state that their measurements "are not too accurate." No reference is made to this difficulty in the article of Bitter *et al.*

[10] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 6, 354.

TABLE I. The susceptibility of copper at various temperatures

Temperature (°K)	Mass susceptibility (cgs units)
300	-0.0830×10^{-6}
77	0.0816
20.2	0.0821
18.1	0.0816
16.3	0.0812
13.8	0.0802
10 ± 1	0.0795
4.187	0.0771
3.003	0.0735
2.155	0.0706
1.450	0.0673

Since de Haas and van Alphen state their results are not too accurate because of damping difficulties, there is little point in looking for further reasons to explain the disparity between their results and those presented in this paper. We do not know the origin of the anomaly found by Bitter *et al.*; however, we observe that the temperature range in which the anomaly appears is just that in which damping problems should become serious.

Our results between room temperature and 1.5°K can be expressed as the sum of a constant diamagnetic susceptibility and a paramagnetic term proportional to $1/T$. About one-fifth of this $1/T$ component results from the nuclear moment of the copper. It would only require 3 parts in 10^7 of a strongly paramagnetic ion such as Fe^{++}, to explain the remainder of the $1/T$ dependence, and this level of impurity is plausible considering the analytical estimates for the paramagnetic impurity content.

Thus it seems likely that the susceptibility of pure copper is substantially independent of temperature, and that the measured temperature dependence in our case is due to impurity. That the temperature dependence in the helium range should be attributed to impurities and not to the copper itself is supported by measurements of the electronic specific heat of copper[11]; in these experiments, γ was found to be independent of temperature in the helium range.

In conclusion, we wish to comment on the search for small anomalies in the susceptibility at low temperatures.[4] It is clear from the analysis of our data that for such measurements, one really requires specimens whose purity is at least an order of magnitude higher than those currently available; otherwise existing anomalies may be masked by the effect of impurities.

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[11] Corak, Garfunkel, Satterthwaite, and Wexler, Phys. Rev. 98, 1699 (1955).