duction of hydrogen again reduces the oxide and allows the iron once again to dissolve in the copper.

CONCLUSIONS

Commercial specimens of copper and brass may be rendered completely non-magnetic by heating in hydrogen to a sufficiently high temperature to allow the magnetic impurity to dissolve in the copper lattice. A temperature of 900°C is safe for a two-hour treatment. This method was unsuccessful in the case of silver, but might work for certain other metals with which iron can form solid solutions. The magnetism can be made to return in copper by reheating in air above 850°C, or by annealing plus cold work.

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Magnetic Properties of Solid Solutions

III. The Paramagnetic Alloys of Copper and Nickel

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The magnetization of the paramagnetic alloys of copper with nickel has been studied as a function of temperature and applied field. It is found that a Curie-Weiss equation cannot represent the results and an equation of the form $\chi = aT + b + (c/T)$ is found to be satisfactory. Alloys in the range from 30 to 38 percent nickel showed a considerable field dependence of the susceptibility at low temperatures.

THE magnetic properties of copper-nickel alloys have been investigated by many people but most of the work has been done at elevated temperatures and on those alloys which are definitely ferromagnetic. The present work was intended primarily to cover the low temperature properties of those alloys which are not ferromagnetic at room temperature, although the investigation was extended to elevated temperatures in order to get a more comprehensive picture of the magnetic behavior. In this alloy series there are compositions which are neither ferromagnetic nor truly paramagnetic even in the Curie-Weiss sense and it is this phenomenon which was looked for in the investigation. It was hoped that such a study would reveal not only the magnetic moment of nickel atoms in dilute solution in copper but also contribute to the knowledge of conditions which lead to ferromagnetism as the concentration of nickel is increased. Copper-nickel alloys are particularly suited for this purpose since they form a complete series of solid solutions in which the added nickel atoms simply replace the copper atoms on the crystal lattice of the latter.

PREPARATION OF ALLOYS

The materials used for the alloys were Mallinkrodt's reagent copper[1] and reagent nickel[2] which were melted together in quantities of about 40 grams. Melting was carried out in an alundum crucible and in a hydrogen atmosphere, the temperature of the furnace being about 1500°C. The alloys were chill cast in a vacuum directly from this melting temperature. These castings were given a homogenizing anneal at 900°C in hydrogen for 36 hours and then were cold swagged with intermediate anneals into the form of $\frac{5}{16}$-inch diameter rods. Short pieces weighing

TABLE I. Composition of alloys, weight percent.

Alloy	Ni	Fe	Alloy	Ni	Fe
J27	—	0.00	J25	20.34	0.016
J7	0.94	0.0023	J24	29.98	0.024
J8	4.99	0.0046	J23	35.59	0.030
J9	10.10	0.0094	J22	38.00	0.029
J26	10.99	0.012	J21	50.16	0.034

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[1] Sb −0.01 percent, As −0.001 percent, Fe −0.004 percent, Pb −0.01 percent, Sn −0.01 percent.

[2] Co −0.01 percent, Fe −0.10 percent, Pb −0.01 percent.

TABLE II. Susceptibility per gram of alloy.

T −°K	Weight percent nickel									
	0*	0.94	4.99	10.1	11.0	20.3	30.0	35.6	38.0	50.2
14.0	−0.034	−0.023	0.125		0.581	1.27	4.37†	14.8†	44.7†	
20.4		−0.032	0.104	0.362	0.483	1.10	3.62†	11.0†	31.5†	
77.3	−0.073	−0.052	0.052	0.216	0.274	0.67	1.81	4.01	7.70†	Ferromag.
295	−0.0796	−0.062	0.042	0.185	0.221	0.553	1.277	1.993	2.84	11.8
523	−0.0786	−0.060	0.047		0.232	0.592	1.222	1.675	2.11	
773	−0.0748	−0.055	0.063		0.262	0.635	1.200	1.561	1.85	
1023	−0.0693	−0.045	0.079		0.300	0.687	1.213	1.515	1.74	
1273	−0.0645	−0.043	0.103		0.339	0.735	1.230	1.497	1.69	

* Copper with 0.0025 percent iron described in preceding paper, Phys. Rev. **60**, 134 (1941).
† Measurements showing field dependence. Initial susceptibility given.

about 4 grams were cut from the rods and were used as the specimens for measurement. Immediately adjacent pieces were cut off for chemical analysis for iron and nickel, the results of which are given in Table I. The specimens were given a final anneal in hydrogen and cooled in the furnace in order to remove the effects of cold work.

METHOD OF MEASUREMENT

The same technique and the same magnet were used for these measurements as has been described in the preceding papers[3] of this series. For measurements below room temperature the specimens were suspended from the balance with a silk thread while a sling made of molybdenum foil was used for this purpose at elevated temperatures. No attempt was made to make a correction for the force on the silk thread but a correction was made whenever the molybdenum sling was used.

EXPERIMENTAL RESULTS

The susceptibility of the alloys was determined by plotting the magnetization against the field and taking the slope of the straight line which is found between 10 and 30 kilogauss. This procedure automatically corrects for any traces of ferromagnetic particles since these always are practically saturated in fields of this magnitude. The ferromagnetic inclusions in all cases were almost negligible.

Certain of the alloys, which were normally paramagnetic at room temperature, began to show progressively larger saturation effects in high fields as the temperature was lowered. As with the copper-iron alloys, this effect was considered to be a true property of the alloy and not just simply the result of ferromagnetic inclusions. In such cases the initial slope of the magnetization curves was taken as the initial susceptibility since the room temperature measurements showed an insufficient amount of ferrromagnetic particles to affect appreciably this quantity. An example of this type of behavior is shown in Fig. 1 for the case of an alloy with about 40 percent nickel.

The values of mass susceptibility as determined by the above methods are given in Table II. The measurements showing field dependence are indicated and for these the initial susceptibility is given.

It is to be noted, as discussed in an earlier paper,[3] that the relative precision of the values given in Table II for different specimens is not greater than about 1 percent because of the difficulty in locating the specimens at exactly the same point in the magnet. On the other hand, the relative accuracy of the values obtained for any given specimen at different temperatures above room temperature is much greater than this, since the position of the specimen was not altered throughout the run. This position could not change appreciably as a result of thermal expansion since the heated zone in the furnace is only a few inches long. This conclusion is of importance in evaluating the small but consistent changes in susceptibility which are observed above room temperature. Fortunately, this conclusion is substantiated by the measurements themselves since it is found that both dia- and paramagnetic susceptibilities change in the

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[3] F. Bitter and A. R. Kaufmann, Phys. Rev. **56**, 1044 (1939); Bitter, Kaufmann, Starr, and Pan, Phys. Rev. **60**, 134 (1941).

proper direction as the temperature is varied; that is, the paramagnetic values become greater when the diamagnetic values decrease. If the observed changes with temperature were due simply to a shift in position of the specimen, then the dia- and paramagnetic susceptibilities would both either increase or decrease depending on the direction of the shift.

DISCUSSION OF RESULTS

The susceptibility at room temperature is plotted as a function of nickel content in Fig. 2, and the results of previous workers are shown for comparison. Our results lie along a smooth curve which is in qualitative agreement with previous measurements[4, 5] except for the work of Williams[6] who found a bulge at about 30 percent nickel. The quantitative agreement of the various workers is not too good. It seems likely that the reason for this is to be found in the purity and treatment of the alloys rather than in the methods of measurement. For example, at room temperature 0.1 percent iron will change the susceptibility of copper to the same extent as 4 percent of nickel and hence the iron impurities of the alloys up to about 20 percent nickel may influence considerably the value obtained for the susceptibility. Above 30 percent nickel the susceptibility increases very rapidly with concentration and, therefore, it becomes increasingly important to be sure that the alloys are well homogenized before measurement. The fluctuation in nickel concentration throughout a specimen as solidified from the liquid state can easily be great enough to give an erroneous value for the susceptibility corresponding to the average composition of the specimen.

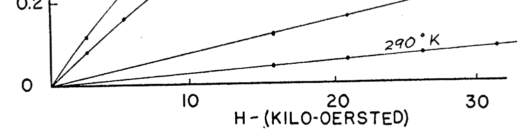

FIG. 1. Magnetization curves [specific intensity of magnetization (σ)] at low temperatures.

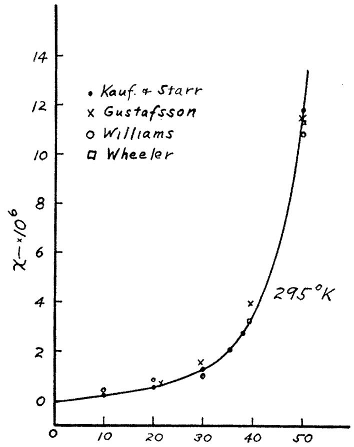

FIG. 2. Mass susceptibility as a function of nickel content at room temperature.

It is not beyond the realm of possibility that at least a partially ordered structure might occur in the composition range of Cu_3Ni and that such an occurrence would affect the susceptibility. This might account for the irregularity in the susceptibility *versus* concentration curve as reported by Williams.[6] In order to check this, the authors slowly cooled the 30 percent nickel alloy from 820°C to 220°C over a period of ten days, since this should allow an ordered structure to form. The susceptibility of this specimen agreed with the value obtained previously to within the experimental error. As a further test the susceptibility of the slowly cooled specimen was measured at 50°C intervals up to 450°C, since the breaking up of an ordered structure should give a discontinuous change in the observed values. No such effect was observed and hence it was concluded that the specimen did not have an ordered structure, or at least that if there were an ordered structure it caused less than a 1 percent change in the susceptibility.

From Fig. 2 it is evident that the susceptibility does not vary linearly with the concentration of nickel and that the deviation from linearity becomes more and more marked as the ferro-

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[4] G. Gustafsson, Ann. d. Physik **28**, 121 (1937).
[5] M. Wheeler, Phys. Rev. **56**, 1137 (1939).
[6] E. H. Williams, Phys. Rev. **38**, 828 (1931).

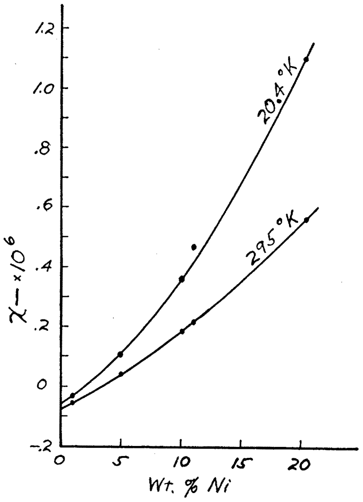

FIG. 3. Non-linear variation of susceptibility with concentration in dilute solutions.

magnetic compositions are approached. This behavior is true at all temperatures down to 14°K and it is true even for small concentrations of nickel as shown in Fig. 3.

The observed low temperature susceptibility values were corrected for the susceptibility of copper and the dissolved iron impurities, and the reciprocals of these quantities were plotted against the absolute temperature as shown in Fig. 4. It is apparent that a Curie-Weiss law does not describe the results for the low nickel alloys and that it tends to become more satisfactory as the nickel content approaches the ferromagnetic compositions. In view of this behavior no attempt was made to calculate Bohr magneton values for the nickel atoms by means of the Curie-Weiss equation although this was done by a different method as will be explained shortly.

Because of the failure of the Curie-Weiss equation to describe the results below room temperature, the measurements were extended to 1300°K. The susceptibility values over the entire range of temperature are plotted in Fig. 5. It is immediately apparent that the susceptibility of all the alloys increases at high temperature, although this effect is concealed by the tendency toward a Curie-Weiss behavior in the higher nickel alloys. This high temperature behavior is undoubtedly the same phenomenon as has already been reported for pure copper[7] although the effect seems to become much greater as nickel is added.

For purposes of comparison the measurements of Gustafsson[4] are also shown in Fig. 5. It is apparent that the temperature range covered by his work did not allow him to observe the phenomenon now reported and that his work is in agreement with ours over the corresponding ranges of temperature.

It is obvious from Fig. 5 that the Curie-Weiss equation cannot represent the results at high temperatures and hence an expression of the form

$$\chi = aT + b + (c/T) \qquad (1)$$

was fitted to the curves by substituting experimental values at three temperatures and solving for the constants. This procedure is quite arbitrary, of course, and can only be justified if the curve calculated from the constants represents the experimental curve accurately. In the present case there was satisfactory agreement between the computed and the experimental curves for all the alloys from 10 to 35 percent nickel. That is, the difference between the two curves was not greater than a few percent except at 14°K. At this temperature and for the other alloys at other temperatures as well, the difference was as large at 10 percent. In spite of this it seems worth while to present briefly the results obtained and accordingly the constants are tabulated in Table III.

The values in Table III were found when the

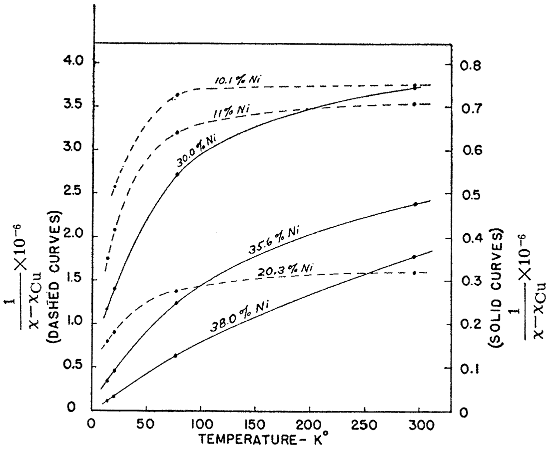

FIG. 4. Reciprocal of mass susceptibility corrected for copper as a function of temperature.

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[7] Bitter, Kaufmann, Starr, and Pan, Phys. Rev. **60**, 134 (1941).

susceptibility data obtained at 20.4°K, 290°K, and 1270°K are used for the simultaneous solutions. A choice of different temperatures would lead to somewhat different values for the constants. Also, if one of the terms in Eq. (1) is small compared with the other terms, then that constant is relatively more subject to error because of the limited experimental accuracy. This reason presumably accounts for the erratic variation of the constants a and b when c becomes large.

The first term in Eq. (1), which indicates an increase in susceptibility with increasing temperature, is not accounted for by any of the present theories of magnetism. Such behavior has been reported, however, for the alkali metals[8] and has been attributed by Stoner to a decrease in the number of electrons per unit volume caused by the thermal expansion of the crystal. This explanation is fairly consistent with the present observations on pure copper since it is possible to calculate a temperature coefficient for the mass susceptibility which is only about six times smaller than the value for a which is given in Table III. This calculation was made with the equation for the susceptibility of free electrons and on the assumption that the change in the number of electrons per unit volume is proportional to the temperature coefficient of thermal expansion for copper. Such a calculation is not nearly as satisfactory for the alloys since the coefficient of thermal expansion changes only slightly with addition of nickel to copper, but the constant a changes by at least a factor of 10 when only 20 percent of nickel is added. However, the other factors which may change with alloying such as the number of free electrons per atom and the shape of the energy band could easily mask any effect due to differences in expansion coefficient.

TABLE III. Constants in Eq. (1) and Bohr magneton numbers (p_B).

Alloy	Wt. percent nickel	$a\times10^{10}$	$b\times10^{6}$	$c\times10^{6}$	p_B
J27A	0.00	0.237*	−0.097*		
J7A	0.94	0.217	−0.071	0.787	0.199
J8A	4.99	0.67	0.017	1.756	0.129
J26A	10.99	1.38	0.160	6.34	0.165
J25A	20.3	2.22	0.444	13.29	0.176
J24A	30.0	0.91	1.073	51.95	0.286
J23A	35.6	0.31	1.302	197.7	0.512
J22A	38.0	5.42	0.510	632.0	0.886

* Values at 290°K, 770°K, and 1270°K used in simultaneous solution.

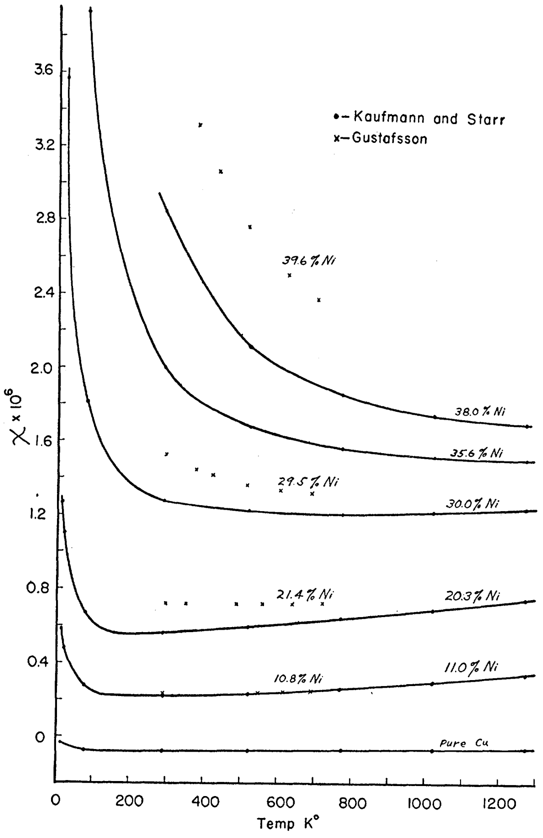

FIG. 5. Mass susceptibility as a function of temperature for different nickel contents.

The constant b of Eq. (1) may be considered as the sum of the diamagnetism and temperature independent electron paramagnetism. It is interesting to note, first of all, that this treatment of the experimental data leads to a value of -0.097×10^{-6} for the temperature independent mass susceptibility of copper instead of the ordinary room temperature value of -0.085×10^{-6} and that this new value is in somewhat better agreement with the calculated value for copper.[9]

The values of b increase continuously with nickel content until c becomes so large that b can no longer be satisfactorily determined. At

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[8] E. C. Stoner, *Magnetism and Matter* (Methuen & Company, London, 1934), p. 509.

[9] E. C. Stoner, *Magnetism and Matter* (Methuen & Company, London, 1934), p. 511.

30 percent nickel b has become about 15 times as large as the theoretical free electron susceptibility of copper. In terms of the band theory of susceptibility this would mean that the number of states at the top of the energy band has increased by this factor since the electronic susceptibility is proportional to the number of states. However, an increase of this magnitude hardly seems compatible with the published energy band shape for copper[10] in spite of the fact that the alloys are approaching an unfilled d band. If the nickel and copper atoms of the alloys form a common set of bands, then the d band should not begin to be unfilled until 40 percent nickel is reached. The present determination of b means either that this perfect sharing of electrons does not occur in the alloy or else one must conclude that b does not have the significance attributed to it here.

The last term in Eq. (1) offers further evidence that a common $3d$ band for the copper and nickel atoms does not describe the results accurately. The reason is simply that this term indicates a normal paramagnetic susceptibility whereas the band picture would alloy only a temperature-independent electronic susceptibility up to 40 percent nickel. There can be no doubt that the low nickel alloys exhibit a large temperature dependence, but whether or not this is correctly represented by a term in $(1/T)$ is open to dispute. At any rate the constant c as here determined shows a continuous variation with nickel content becoming rapidly larger as a concentration of 40 percent is approached. If one regards c as the ordinary Curie constant, the Bohr magneton values per nickel atom may be obtained from the formula $p_B = 2.84(cM/K)^{\frac{1}{2}}$, where M is the molecular weight of nickel and K is the fraction of nickel by weight in the alloy. From Table III it can be seen that the Bohr magneton values remain fairly constant up to about 20 percent nickel and then increase rapidly. The significance of this is not clear since the values of p_B are about ten times smaller than that found for pure nickel above its Curie temperature.

Finally, we must discuss the field dependence of the susceptibility which was observed at low temperatures in the alloys with 30 percent and more of nickel. The careful measurements of Weiss and Forrer[11] have shown that the magnetization curve of pure nickel shows no discontinuity at the Curie temperature and that the curve becomes linear within the experimental error only after 40 degrees above the Curie temperature has been reached. It seems reasonable to suppose that this same phenomenon exists also in the ferromagnetic copper-nickel alloys. From this it follows that in varying the composition from ferrromagnetic to paramagnetic alloys at any given temperature the paramagnetic compositions close to the boundary will show field dependence. Our observations must be part of this phenomenon in spite of the fact that the Curie temperature has been supposed to reach absolute zero at 40 percent nickel.

The ordinary Weiss theory will lead to a large field dependence of the susceptibility above the Curie temperature as may readily be verified by numerical substitution in the equation. For nickel this calculated field dependence becomes smaller than 1 percent at 30°C above the Curie temperature and this is in agreement with the measurements. (The calculated magnetization, however, is only about one-half as large as the measured values in fields up to 20,000 oersted.) This result substantiates the idea that the observations on low nickel alloys are to be correlated with the tendency toward ferromagnetism. A more detailed discussion of this problem will be undertaken at a later time after more observations of the same sort have been made on similar alloy systems.

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[10] J. C. Slater, Phys. Rev. **49**, 537 (1936).

[11] P. Weiss and R. Forrer, Ann. de physique **5**, 153 (1926).