each W when D_0 is in angstroms. Table I also shows a comparison of the results here obtained with those of Bardeen and the image force law. The former values were computed from the relation[7]

$$W=-(e^2\langle R_1^2\rangle_{\text{Av}}/12D_0^3)(Ce^2/2r_sh\nu_1/1+Ce^2/2r_sh\nu_1)$$

developed by Bardeen, and the latter were obtained from Eq. (1). The agreement with Bardeen's theory appears on the whole satisfactory, although the values obtained from the latter are always lower than ours. Table II contains similar data for divalent metals.

The interaction between the metal ions and the visiting molecule is of course included in the basic formulas (9) and (11). But the approximations made in evaluating $A^{(2)}$ and $\Delta E_{\text{Av}}^{(2)}$ ignore this effect. It is therefore of interest to calculate it separately in order to exhibit its order of magnitude. This was done by the methods of reference 4 for the metal Na only. The interaction energy is also proportional to D_0^{-3}; the coefficient, in the same units as the others, is given in the last column of Table I. Clearly, this effect is generally negligible in comparison with that expressed by Eq. (12).

JULY 15, 1941 PHYSICAL REVIEW VOLUME 60

Magnetic Studies of Solid Solutions

II. The Properties of Quenched Copper-Iron Alloys

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(Received April 28, 1941)

The alloys of copper and iron which have been studied show unusual magnetic properties both in the saturation effects at low temperatures and in the apparent change in the magnetic moment of the dissolved iron atoms over the range of temperatures from 14°K to 1300°K. Further research is required on other alloy systems containing transition elements dissolved in the noble metals in order to ascertain whether the phenomena are due to fundamental magnetic properties or due to the state of aggregation of the iron atoms.

In the first paper of this series[1] the authors described a method of measurement which has been used again for the present experiments. The only difference in this case is that the location of the specimen in the magnet has been changed slightly in order to have stable equilibrium and that the furnace of Fig. 2, Part I, has been replaced by a Dewar flask for low temperature measurements. The specimens were in an atmosphere of hydrogen for all experiments except those below 60°K for which a mixture of hydrogen and helium was used.

Some preliminary results presented in Part I on alloys of copper with small percentages of iron showed that the magnetic properties depended in a complicated way on the heat treatment of the specimens. In an effort to narrow the range of investigation, the present experiments have been confined to that state of the alloys in which all the iron is believed to be in solid solution. This state surely exists in the high temperature measurements above the solubility limits and it is assumed to exist for all the present experiments at room temperature and below because each of the specimens was quenched in water from above the solubility limits.

The alloys for this investigation were made by dissolving iron in molten electrolytic copper in an atmosphere of hydrogen and then chill casting in vacuum. The castings were annealed for 5 days at 1000°C and then quenched after which they were swaged to the desired size. Samples for measurement were cut from this stock and prepared by annealing the low iron alloys at 950°C and the

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[1] F. Bitter and A. Kaufmann, Phys. Rev. 56, 1044 (1939).

alloys with more than 0.5 percent iron at 1030°C for 24 hours and then quenching in water.

Susceptibility measurements at room temperature on these specimens showed the absence of any appreciable ferromagnetism except for the alloy with 2.7 percent iron which had a ferromagnetic moment per unit mass of 0.02 absolute unit. This moment corresponds to less than 0.4 percent of the total iron in the specimen but this value indicates, nevertheless, that the solution heat treatment in this case was not entirely successful, possibly because of an insufficiently rapid cooling rate. The absence of ferromagnetism in the other specimens indicates that the iron is entirely in solution.

Experimental Results

The susceptibility values at room temperature increase rapidly with composition up to 0.7 percent iron and then show little further change at higher compositions as shown by curve *A*, Fig. 1. This peculiar behavior above 0.7 percent iron indicates either that the randomly distributed iron atoms have affected each other in some way or else that the quench has not retained the iron atoms in a random arrangement. The second possibility seems the more plausible for two reasons. In the first place, if randomly distributed iron atoms could influence each other so strongly at room temperature, then some trace of the phenomenon ought to still exist at high temperatures. However, curve *B* shows only a linear increase of susceptibility with iron content at 1300°K, a temperature which is above the solubility limit for all the alloys. In the second place, it is known from the observations in Part I that an incipient or actual precipitation of iron will cause a decrease in susceptibility without the appearance of ferromagnetic iron. Such a condition in the quenched alloys would lead to the observed behavior and would mean simply that the quenching treatment was not entirely effective for iron contents greater than 0.7 percent. Because of this conclusion, the state of the quenched alloys with more than 0.7 percent iron was considered to be doubtful and accordingly only a few low temperature measurements were made on them and none of these results are discussed in the following.

The susceptibility of the quenched alloys showed a large temperature dependence below room temperature as would be expected from the high temperature results in Part I. The interpretation of the data is not straightforward, however, since the susceptibility values showed a considerable field dependence. The extent of this phenomenon is shown by Fig. 2 where the magnetization curves for the specimen with 0.7 percent iron are plotted. The heavy lines going through the points represent the experimental data while the lighter, straight lines show the slope at the origin. Measurements were made up to 30 kilogauss but no definite saturation effects were found even at 14°K. This fact combined with the absence of field dependence at room temperature indicates that the observed behavior cannot be due simply to the presence of ordinary ferromagnetic impurities. From Fig. 2 it can be seen that at a given composition the field dependence becomes greater as the temperature is lowered while other observations show that at a fixed temperature the field dependence becomes less as the iron content decreases. At 14°K the most dilute alloy which still showed a definite field dependence contained about 0.1 percent iron. It is perhaps well to mention that the results shown in Fig. 2 were reproducible, thus removing the possibility that some permanent change in the specimen such as the precipitation of iron during cooling might have caused the observed behavior.

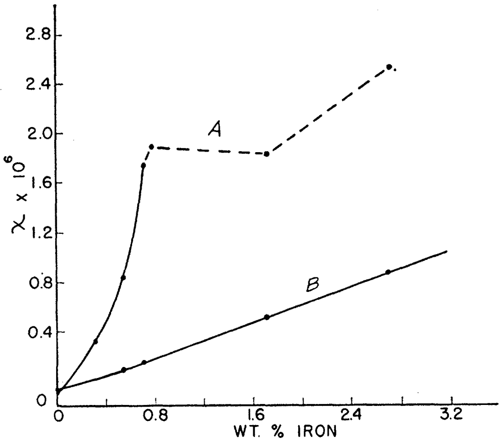

FIG. 1. Mass susceptibility of copper-iron alloys. Curve *A*—quenched alloys at room temperature. Curve *B*—alloys at 1300°K.

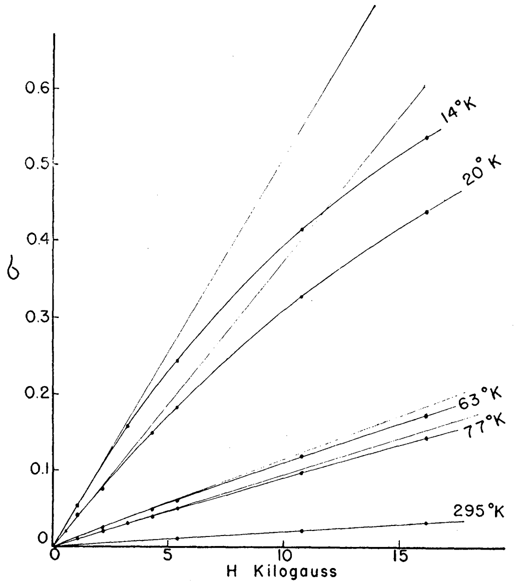

FIG. 2. Magnetization curves of quenched copper containing 0.7 percent iron.

In all cases where a field dependence was observed, the initial susceptibilities as indicated by the straight lines in Fig. 2 were determined. These values as well as those obtained by orthodox methods at higher temperatures are given in Table I.

The susceptibility of "pure" copper was measured over the same temperature range as the alloys in order to be able to make a correction for it. Some typical results are plotted in Fig. 3 and are tabulated in Table I. All the samples showed a nearly linear decrease in diamagnetism between room temperature and 1000°C as mentioned in Part I, but below room temperature the measurements showed a considerable divergence. The first specimens examined were made of the copper used in the alloys and these showed a large change toward paramagnetism at low temperatures. A calculation indicated that the paramagnetism of the dissolved iron impurities could cause this behavior but in order to be sure a sample containing less than 0.00007 percent iron was also measured.[2] The increase in susceptibility at low temperatures in this case cannot be accounted for by the iron or even by the other impurities such as manganese because of the extremely high purity of the copper. The observed behavior is apparently a property of pure copper but further investigation is required to prove this. The values for "pure" copper that were finally used were obtained by extrapolating the curves in Fig. 4 to zero iron content.

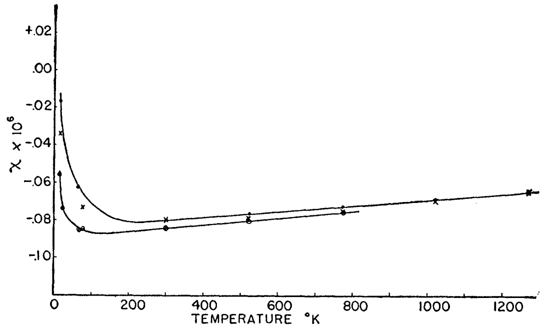

FIG. 3. Susceptibility of "pure" copper. —●— 0.0082 percent iron; —X— 0.0025 percent iron; —⊙— <0.00007 percent iron.

DISCUSSION OF RESULTS

The susceptibility values in Table I between 14°K and 77°K may be represented by an equation of the form

$$\chi = \chi_{\mathrm{Cu}} + C/(T-\theta) \tag{1}$$

as shown by Fig. 5 in which percent iron/$(\chi - \chi_{\mathrm{Cu}})$ is plotted as a function of temperature. From the slopes of these lines one can evaluate the constant C and from this the Bohr magneton value per

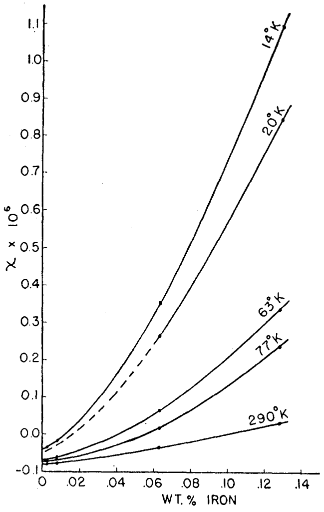

FIG. 4. Mass susceptibility of dilute copper-iron alloys below room temperature.

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[2] Obtained through the courtesy of Dr. A. J. Phillips of the American Smelting and Refining Company. The specimen contained 99.998 percent copper and a typical analysis is given in A.I.M.E. Tech. Pub. 1289 (1941).

iron atom can be calculated by using the equation

$$p_B = 2.84(100M/C)^{\frac{1}{2}},$$

where M is the gram atomic weight of iron. The results are given in Table II along with the values of θ, the paramagnetic Curie temperature.

The Bohr magneton values seem to vary linearly with composition although the sample with 0.5 percent iron forms an exception to this. The fact that the 0.7 percent iron specimen has a Bohr magneton value almost equal to the theoretical value for a free, doubly ionized iron ion probably has no special significance in view of the large field dependence of susceptibility. The small values of θ indicate that the initial susceptibility of the dissolved iron atoms behaves almost like that of a perfect Curie substance. According to the usual theories this behavior would indicate that the influence of the iron atoms upon each other is very small.

The experimental data do not lie on the curves of Fig. 5 at high temperatures. This can be seen for the room temperature values in Fig. 5 and more completely from the values obtained above the solubility limits as shown in Fig. 6. No measurements were made in the intervening temperature range because a precipitation of iron would have occurred.

The interesting thing about the high temperature data is that they can also be represented by Eq. (1) but in a way which indicates a different behavior from that at low temperatures. The slopes of all the high temperature curves are almost equal, which means that the magnetic moment per iron atom is the same in all the alloys. This magnetic moment corresponds to a Bohr magneton value of 4.7, which happens to be the theoretical value for an iron ion in which the electron spins only are contributing to the moment. The extrapolated Curie temperatures are considerably larger in magnitude than those found at low temperatures and they change progressively from negative to positive values as the iron content is increased.

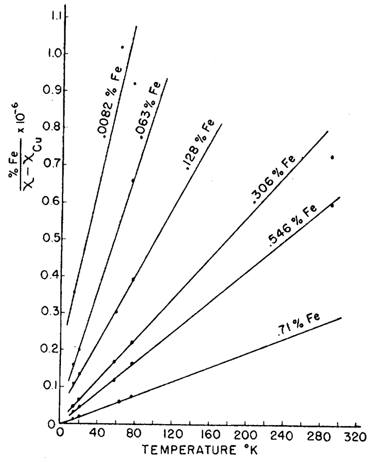

FIG. 5. Reciprocal of susceptibility per gram of iron below room temperature.

The high temperature data indicate that the iron atoms have a definite magnetic moment when dissolved in copper and that this moment is independent of concentration over the range investigated. Furthermore, the decrease of Curie temperature from positive to negative values may be attributed to a decreasing interaction of some sort between the iron atoms as the iron content becomes less, although the ordinary

TABLE I. *Susceptibility per unit mass*—$\chi \times 10^6$.

T° K	PURE COPPER	Weight Percent Iron 0.0025	0.0082	0.063	0.128	0.306	0.546	0.71	1.70	2.69
14.0	−0.056	−0.034	−0.017	0.356	1.10	6.4	15.6	51.0		
20.4	− .074			.263	.845	4.52	12.4	37.5		
58					.338	1.75	4.57			
63.1	− .0863		− .062					11.4		
77.3	− .0850	− .073	− .066	.0197	.238	1.29	3.26	9.42		
295	− .0843	− .0796	− .080	− .033	.0354	.328	.823	1.74	1.82	2.52
380					.0117	.237	.596			
523	− .0809	− .0786	− .0761							
773	− .0760	− .0748	− .0732							
1023		− .0693								
1073		− .0685	− .0685		− .0314	.0346	.1205	.240		
1173		− .0665	− .0665		− .0316	.0292	.1066	.183		
1273		− .0645	− .0646		− .0321	.0251	.0965	.163		
1298									.506	.875

Weiss theory would allow θ only to approach zero but not to become negative. It is interesting to note that the measurements of Gustafsson on manganese dissolved in copper show the same type of variation of Curie temperature with concentration and likewise a constant value for the magnetic moment of the manganese atoms.[3]

The results at low temperatures, as already mentioned, show a different behavior of the iron atoms in that the magnetic moment increases rapidly with concentration while the Curie temperatures are so small as to indicate only a slight mutual influence of the iron atoms. This behavior is difficult to understand with the Curie-Weiss theory and in addition the apparent change in the state of the iron atoms between high and low temperatures is most unusual in magnetic phenomena. Since the alloys at low temperatures were supersaturated, the question arises as to whether or not this condition could produce the observed behavior. This possibility is somewhat discredited by the fact that the most dilute alloys which, of course, are the least supersaturated, still show the same type of change. In order to settle the problem of whether supersaturation produces the above effect or whether it is a real magnetic phenomenon, it would be necessary to examine other similar alloys both supersaturated and in equilibrium.

The dependence of susceptibility upon field strength at low temperatures is further evidence of a peculiar magnetic behavior. The observed effect is much too great to be accounted for by the saturation of an ordinary paramagnetic substance even at 14°K. It is conceivable that the quenching treatment did not succeed in keeping the iron atoms distributed at random and hence that they had formed local regions of high concentration. Such groups of iron atoms might be on the verge of becoming ferromagnetic and hence could show saturation effects in a strong field. This situation seems unlikely, however, since by plotting magnetization against H/T all the curves from 77°K to 14°K can be brought into coincidence, as would be expected for a paramagnetic substance but not for a substance in which interactions have almost produced an intrinsic magnetization.

TABLE II. *Curie temperatures* (θ) *and Bohr magneton per atom* (p_B).

WT. % Fe	p_B	θ
0.0082	2.0	-16
0.063	2.4	-6
0.128	3.1	-10
0.306	4.1	-4
0.546	4.7	-2
0.71	6.9	0

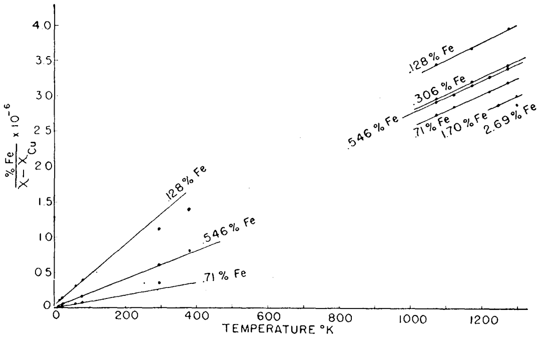

FIG. 6. Reciprocal of susceptibility per gram of iron for quenched alloys below room temperature and for the alloys above the solid-solubility temperature.

Another possible way of accounting for the field dependence would be to assume that the iron has actually formed in numerous small regions which are spontaneously magnetized to some fixed intensity. If the orientation of these magnetic moments in an external field was given by the Langevin function as for a paramagnetic gas, then the magnetization would depend upon H/T as found, and since each region would have a large moment compared with a single atom, $\mu H/KT$ could be large enough to give an ordinary paramagnetic saturation effect. There seems to be no way of proving or disproving this idea and hence one can question it only on the basis of the complicated and somewhat unreasonable mechanism required.

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[3] E. Vogt, Ann. d. Physik **29**, 362 (1937).