Superparamagnetism, Nonrandomness, and Irradiation Effects in Cu-Ni Alloys*

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The effect of neutron irradiation on copper-nickel alloys has been investigated by means of magnetic susceptibility measurements. The susceptibilities were measured by the Gouy method between 300°K and 2.0°K for a series of alloys ranging from 17.22 to 46.5 atomic percent nickel. It is shown that without superparamagnetism an unreasonable magnetic moment per nickel atom has to be assumed. This model is confirmed by irradiation studies in which samples were exposed to neutron fluxes at the Brookhaven reactor, ranging up to 2.2×10^{19} neutrons/cm^2 while at 80°C, and the magnetic susceptibilities were found to increase following the irradiation. The increase was easily observable due to its strong temperature dependence, and was greatest for the samples with the highest nickel content and for samples exposed to the highest neutron fluxes. The susceptibilities of the alloys returned to their original values following an anneal in or above the temperature range where self-diffusion becomes important, while no changes in the susceptibilities were observed following anneals at lower temperatures. It is suggested that the copper-nickel system is not a perfect random solid solution but tends toward segregation, and that the neutron irradiation enhances diffusion toward a true equilibrium at room temperature. This is in agreement with several other observations.

I. INTRODUCTION

THE copper-nickel alloy system is of particular interest for magnetic studies because a transition from ferromagnetic to nonferromagnetic behavior is contained near the center of the composition range and because all compositions are thought to be random solid solutions with face-centered cubic structures. Recent measurements[1,2] of the magnetic susceptibilities of these alloys have demonstrated that the anomalous temperature dependence reported by earlier workers was due to ferromagnetic impurities. It is now known that the susceptibilities of alloys containing less than about 27% nickel are essentially temperature independent and increase with nickel content, while alloys with nickel content greater than 27% show an increase in susceptibility at lower temperatures which can be only roughly described by a $1/T$ law. Figure 1 illustrates the previous data[1] combined with new additional results for a sample containing 46.5 atomic percent nickel. The indicated Curie temperatures were obtained from Ahern's[3] interpolation between his and Arrott's[4] measurements.

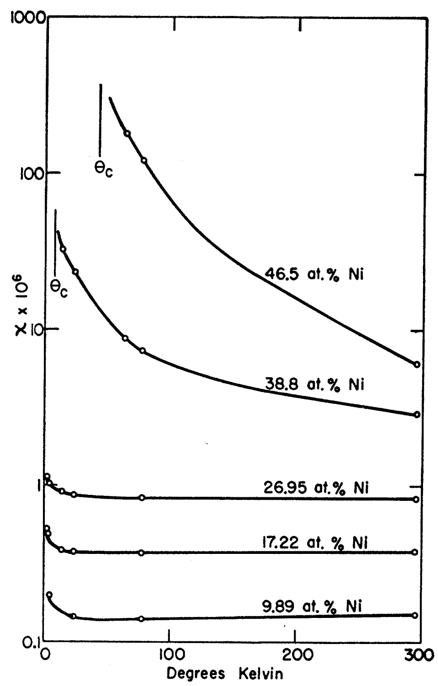

FIG. 1. Magnetic susceptibility as a function of temperature for copper-nickel alloys. Vertical lines indicate approximate positions of Curie temperatures (see text).

Copper-nickel alloys were chosen for the present work because of the strong dependence of the magnetic susceptibility on composition, particularly near the Curie temperature, as illustrated in Fig. 2. It was anticipated that magnetic measurements would permit the detection of variations in atomic distribution which could not be observed by other means.

It is well known that neutron irradiation enhances diffusion in solids, both by local heating and by the production of vacancies and interstitials in excess of their equilibrium values.[5] It is thus possible, in certain cases, to accelerate diffusion in solids toward equilibrium distributions which otherwise might form only very slowly or not at all. A typical example here is the formation of short-range order in alpha brass and also in

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[1] E. W. Pugh and F. M. Ryan, Phys. Rev. **111**, 1038 (1958).
[2] Pugh, Coles, Arrott, and Goldman, Phys. Rev. **105**, 814 (1957).
[3] Ahern, Martin, and Sucksmith, Proc. Roy. Soc. (London) **248**, 145 (1958).
[4] A Arrott, thesis, Carnegie Institute of Technology, 1954 (unpublished); J. E. Goldman and A. Arrott, Phys. Rev. **94**, 782 (1954).
[5] G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957), p. 117.

Cu-Al alloys by neutron irradiation.[6–11] In the present work an attempt was made to determine whether any variations from randomness could be detected in the copper-nickel system under the influence of this enhanced diffusion. It was also anticipated that such observations would give an insight into the nature of the magnetic interactions within these alloys.

II. EXPERIMENTAL TECHNIQUE

The preparation of the 17.22 and 26.95% nickel samples from American Smelting and Refining Company copper, rated at 99.999% pure, and Johnson Matthey spectroscopic grade nickel, rated at better than 99.997% pure, has been described previously.[1] The pure metals were alloyed in evacuated quartz tubes and agitated for 30 minutes in the molten state to assure proper mixing. The melt was then quenched in water to minimize long-range segregation, and the ingots were swaged into cylindrical specimens. The specimens were then heavily pickled in nitric acid and homogenized at 70°C below the solidus for 100 hours.

Since the melting temperatures of the 38.8 and 46.5% nickel samples were too high to be alloyed in quartz, they were obtained from the International Nickel Company where they were produced in a vacuum furnace using a graphite crucible. A spectrographic analysis of these alloys indicates that they have impurities of less than one part per million of iron, cobalt, and manganese. After receiving these specimens they were heavily pickled and homogenized at 1150°C for 120 hours. Chemical analyses performed on the samples agreed with the alloy compositions to within one percent.

Prior to irradiation, the samples were sealed in individual evacuated quartz tubes to prevent surface contamination. The samples were then irradiated in the Brookhaven National Laboratory reactor where they were subjected to a broad spectrum of fission neutrons at a total flux rate of 6×10^{12} *nv* for varying periods of time. During the irradiation the samples assumed the temperature of the pile which averaged 80°C.

The samples were placed in evacuated quartz tubes for each annealing run in order to maintain a clean surface and prevent oxidation. The annealing temperatures were held within ±5°C over the range of temperatures used. After every three isothermal anneals and subsequent susceptibility measurements, the samples were very lightly pickled in nitric acid to reduce the effect of surface contamination due to handling. Care was taken to not remove enough metal to give a measurable change in the susceptibility due to an altering of the sample dimensions.

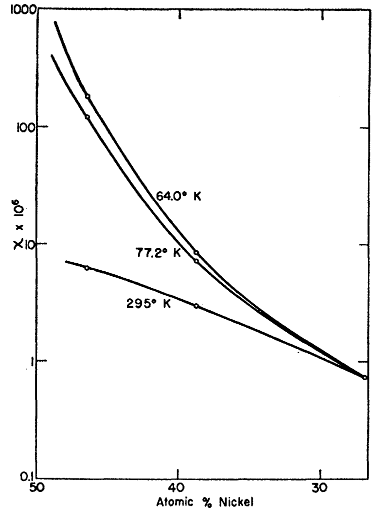

FIG. 2. Isothermal variation of the magnetic susceptibility with composition for copper-nickel alloys. At 64°K and 77.2°K alloys above about 50% Ni and 65 Ni, respectively, are ferromagnetic.

Susceptibility measurements were made by a previously described Gouy balance[2] using fields ranging from 4000 to 23 000 oersted. The samples had the form of wires six inches in length and were fastened to a six inch long, $\frac{1}{4}$-in. diameter cylinder of Pugh's nonmagnetic alloy[12] to prevent bending or swinging of the sample in the magnetic field.

III. EXPERIMENTAL RESULTS

A list of the samples used and the corresponding total neutron fluxes they received may be seen in Table I. The results of the susceptibility measurements are listed in Table II. On Fig. 3 are plotted the fractional increases in the susceptibilities for the 26.95, 38.8, and 46.5% nickel samples which were subjected to the greatest total neutron fluxes. The typical temperature dependence of the increase in the susceptibility observed in the alloys can be seen on this plot, along with the dependence on composition. No detectable increase in susceptibility was found in the 17.22% nickel sample following irradiation of up to 2.2×10^{19} neutrons/cm². With the accuracy obtainable this means that any increase that might have occurred following the irradiation was less than one percent, down to 2°K. For no sample, either before or after irradiation, was any field dependence observed.

TABLE I. Designation of samples and irradiation fluxes.

Number	Composition	Total neutron flux
1	Cu+38.8 at. % Ni	0.725×10^{19} *n*/cm²
2	Cu+38.8 at. % Ni	1.45×10^{19}
3	Cu+38.8 at. % Ni	2.18×10^{19}
4	Cu+46.5 at. % Ni	0.725×10^{19}
5	Cu+46.5 at. % Ni	1.45×10^{19}
6	Cu+46.5 at. % Ni	2.18×10^{19}
7	Cu+17.22 at. % Ni	2.18×10^{19}
8	Cu+26.95 at. % Ni	2.18×10^{19}

[6] Rosenblatt, Smoluchowski, and Dienes, J. Appl. Phys. **26**, 1044 (1955).
[7] Feder, Nowick, and Rosenblatt, J. Appl. Phys. **29**, 984 (1958).
[8] A. C. Damask, J. Phys. Chem. Solids **4**, 177 (1958).
[9] M. S. Wechsler and R. N. Kernohan, J. Phys. Chem. Solids **7**, 307 (1958).
[10] A. C. Damask and G. J. Dienes, J. Phys. Chem. Solids (to be published).
[11] B. L. Averbach, J. Appl. Phys. **30**, 1525 (1959).
[12] E. W. Pugh, Rev. Sci. Instr. **29**, 1118 (1958).

TABLE II. Susceptibility of copper-nickel alloys (cgs mass units×10[6]) before and after irradiation.

Temp.	Before irrad.	After irrad.	Before irrad.	After irrad.	Before irrad.	After irrad.	Before irrad.	After irrad.
	Sample 1		Sample 2		Sample 3		Sample 4	
295°K	+2.92	+3.06	+2.95	+3.10	+2.90	+3.09	+6.07	+6.24
77.2°K	+7.22	+8.83	+7.25	+9.10	+7.21	+9.20	+117	+136
64.0°K	+8.47	+10.47	+8.52	+10.85	+8.59	+11.29	+178	+210
	Sample 5		Sample 6		Sample 7		Sample 8	
295°K	+6.21	+6.56	+6.10	+6.48	+0.381	+0.380	+0.832	+0.836
77.2°K	+123	+156	+120	+158	+0.362	+0.361	+0.8275	+0.830
64.0°K	+183	+244	+179	+248				
20.4°K					+0.373	+0.373	+0.874	+0.908
14.0°K					+0.383	+0.382	+0.899	+0.933
4.2°K					+0.482	+0.480	+1.022	+1.131
2.1°K					+0.528	+0.526	+1.132	+1.258

After the post-irradiation susceptibilities had been measured, the samples were subjected to a series of isochronal annealings at various temperatures. The results of the susceptibility measurements taken after each anneal are listed in Table II. The annealing spectrums of two 46.5, two 38.8, and the one 26.95% nickel sample are shown on Fig. 4. Each point represents a susceptibility measurement performed following a 50-hour isothermal anneal at the indicated temperatures. The susceptibility measurements plotted were those obtained at the lowest measurement temperature. It was found that the annealing phenomenon was independent of the initial neutron flux or the susceptibility measurement temperature. The maximum rate of the annealing process occurs at 250°C, 310°C, and 325°C for the 26.95, 38.8, and 46.5% nickel samples, respectively. This is just the "Tammann" temperature range in which during a typical annealing period the self-diffusion of the atoms begins to be significant. Its variation with composition is in the right direction.[13] No measurable decrease in susceptibility occurs until about 175, 275, and 300°C for the three compositions. The values of the susceptibilities of the samples after annealing at temperatures higher than 350°C agreed with the pre-irradiation values within the experimental accuracy of one percent. Figure 5 shows the fractional increase in susceptibility for the 38.8 and 46.5% nickel samples as a function of the irradiation flux. A deviation from linearity between the change of susceptibility and flux is clearly indicated for fluxes near or below 10^{19} neutrons per cm^2. This corresponds to the displacement of the order of a few percent of the atoms. Such early nonlinearities have been previously observed.[14,15] Due to the level of the induced radioactivity of the samples and the necessary handling before and after susceptibility measurements, the use of higher fluxes was excluded and thus a saturation of the observed changes was not obtainable.

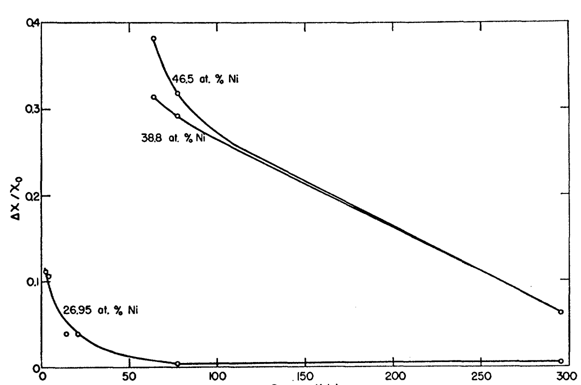

FIG. 3. Relative increase in magnetic susceptibility as a function of temperature following an irradiation flux of 2.2×10^{19} neutrons/cm^2.

[13] G. Grube and A. Jedele, Z. Elektrochem. **38**, 799 (1932).

IV. DISCUSSION OF RESULTS

A. Superparamagnetism

Before discussing the observations on the influence of irradiation on the paramagnetic properties of the copper-nickel alloys, it is necessary to consider the alloys in their normal condition. From Fig. 1 one concludes that in alloys with 38.8 and 46.5 atomic percent nickel the susceptibility is proportional to $C(T-\theta)^{-1}$ according to the Curie-Weiss law. The constant C is about 0.5×10^{-3} cgs mass units × degree for the 38.8 alloy and around 6×10^{-3} for the 46.5 alloy. If we make the extreme assumption that each atom of dissolved nickel contributes 0.6 Bohr magnetons, then the usual formula $C=NJ(J+1)g^2\mu_B{}^2/3k$, where N is the number of nickel atoms per unit mass of the alloy, yields 1.2×10^{-3} and 1.5×10^{-3} for the two compositions, respectively.

In order to account for the higher measured value of C for the 46.5 alloy, each atom of nickel would have to possess 1.7 Bohr magnetons which is most unlikely. It seems much more reasonable to assume that this alloy behaves superparamagnetically, that is, that there are small local clusters sufficiently rich in nickel in which all spins are coupled ferromagnetically to each other and form one domain, but that the temperature is high

[14] G. H. Kinchin and R. S. Pease, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 1.
[15] T. H. Blewitt and R. R. Coltman, Acta Met. **2**, 549 (1954).

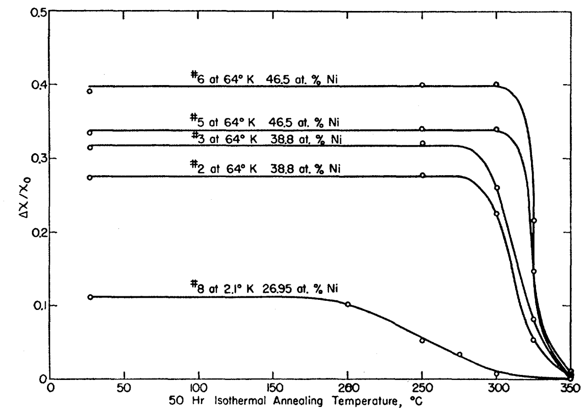

FIG. 4. Isothermal annealing of the relative increase in magnetic susceptibility. Susceptibilities measured at lowest temperature.

enough to provide a short relaxation time for the change of orientation of the resulting spin system. Such a model has been analyzed theoretically by Néel[16] and Bean[17,18] and successfully applied to copper-cobalt alloys by Becker.[19] The main difference between the Cu-Co and the Cu-Ni system lies in the fact that in the former the ferromagnetic particles are discrete precipitates, while in the latter we assume clusters in a solid solution. The possible role of local fluctuations in composition in this alloy has been frequently suggested[20,21] and applied to the interpretation of temperature variation of their electrical resistance.[21]

A quantitative evaluation of the theory for the copper-nickel system is exceedingly difficult because, even if we assume a perfect random solution, there is a continuous distribution of various sizes and compositions of clusters, and each has a different criterion for becoming a superparamagnetic domain. The necessity for a single domain behavior, and for a short relaxation time of the domain orientation, requires the knowledge of the Bloch wall energy and of the anisotropy constant K as a function of composition. Besides this, each composition will have a different contribution per nickel atom to the resultant spin. One can ask, however, what is the *minimum* size of a pure nickel cluster which would account for the observed constant C if all the nickel atoms were in such clusters. If each nickel atom in such a cluster is assumed to contribute 0.6 Bohr magneton then the minimum clusters would contain about 16 atoms each. This is one or two orders of magnitude below the lower limit of the size of precipitates considered in the copper-cobalt system. The minimum size of nickel-rich clusters containing some copper atoms would, of course, have to be larger. For instance, clusters having 60 or 50% nickel would have to contain at least 85 or 175 atoms, respectively, to account for the observed C. In a random solid solution of 46.5 atomic percent nickel the probability of the occurrence of such clusters[21] is of the order 10^{-5}, 10^{-4}, and 10^{-1}, respectively, and thus only the latter can play a role. All of these clusters are sufficiently small that appreciable saturation would not occur in the presence of the applied fields, and no field dependence of the susceptibility should be detected.

The above minimum cluster sizes have been determined by assuming that each cluster has a Curie temperature and moment per unit volume identical to those of larger samples of the same composition. This is actually not true, for it can readily be shown that the smaller the cluster of a given composition the lower will be both its Curie temperature and its moment per unit volume. Since the sample contains clusters of various sizes and compositions, the sample parameter C, defined as $d\chi/d[1/(T-\theta)]$, will, in effect, decrease with increasing temperature. A rough estimate of the Curie temperature θ_a of a cluster or aggregate can be obtained if one assumes that the surface atoms make only half as many ferromagnetic exchange interactions as do the atoms in the inside of the cluster.[22] One obtains then that $\theta_a/\theta_c = 1-1.5r^{-1}$, where θ_c is the Curie temperature of the bulk alloy of the composition of the cluster, and r is the radius of the cluster expressed in terms of the distance between nearest neighbors. For the three kinds of minimum size clusters discussed above, one obtains $\theta_a = 265$, 138, and 77°K, respectively. The larger the cluster of a given composition, the higher its Curie temperature. It follows that in order to explain, for instance, a high value of C at 250 or 300°K for a typically 50:50 random alloy, one cannot consider pure nickel clusters because their occurrence even for the minimum size is too unlikely, nor can one consider clusters close to the average composition because their Curie temperature is too low. At these temperatures

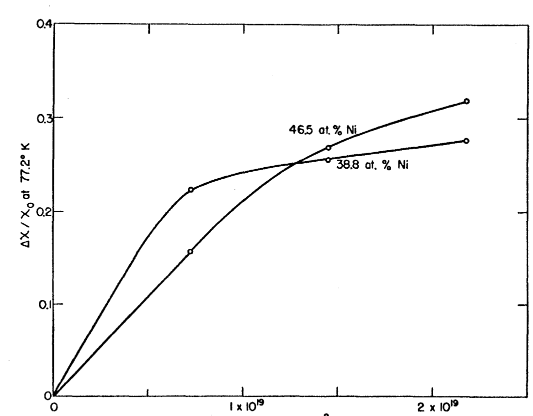

FIG. 5. Relative increase in magnetic susceptibility as a function of neutron flux.

[16] L. Néel, Compt. rend. **228**, 664 (1949).
[17] C. P. Bean, J. Appl. Phys. **26**, 1381 (1955).
[18] C. P. Bean and J. D. Livingston, Suppl. J. Appl. Phys. **30**, 120 (1959).
[19] J. J. Becker, Trans. Am. Inst. Mining Met. Engrs. **209**, 59 (1957), and **212**, 138 (1958).
[20] E. P. Wohlfarth, Proc. Roy. Soc. (London) **195**, 434 (1949).
[21] R. Smoluchowski, Phys. Rev. **84**, 511 (1951).
[22] E. Kneller, Z. Physik **152**, 574 (1958).

probably the only significant contribution to paramagnetism would come from clusters having not less than 65 atomic percent nickel and of such size that their probability of occurrence is less than 10^{-3}. This however is not enough to account for the observed C.

The above considerations lead to the conclusion that the copper-nickel alloys are not random below room temperature but show a tendency to clustering ("Nahentmischung"). This would increase the probability of the occurrence of nickel-rich and copper-rich clusters to values which would agree with the observed paramagnetism. For instance, a segregation with maximum clustering probabilities near 30 and 70 atomic percent at 250°K leads to a probability of about 0.4 for clusters having between 65 and 75% nickel and 50 atoms in each. The corresponding C is about 5×10^{-3} which is quite reasonable. Whether these alloys actually segregate into thermodynamically distinct nickel-rich and copper-rich phases rather than form clusters within one solid solution is impossible to ascertain at the present time. The magnitude of the observed effects, however, seems to favor the first alternative. One would expect the miscibility gap to be centered around the 50:50 composition and extend further into the nickel-rich side than into the copper-rich side. This asymmetry, which is similar to the asymmetry of ordered phases,[23,24] follows from the fact that a nickel atom joining a cluster of nickel atoms would lower its energy by an additional amount of about $k\theta_c/2$ if the cluster were ferromagnetic, and this energy is comparable to the energy of "unmixing."

These conclusions about the nature of paramagnetism in the copper-nickel alloys and about the nonrandom nature of these alloys are strikingly confirmed by the results of irradiation discussed below.

B. Irradiation Effects

There are several ways in which irradiation could, in principle, change the magnetic susceptibility of a metallic solution: One of the most obvious is a chemical change produced by nuclear transmutation. Another possibility is the introduction of stable point defects or their clusters, which would modify local interatomic distances, and thus the local exchange integrals, as well as produce variations of local chemical composition. Finally, the presence of mobile defects and the resulting increase of diffusivity during irradiation may lead to changes in the distribution of the atoms or, in other words, to a change in the frequency of occurrence of various composition fluctuations in an essentially normal crystalline lattice. Additional complications would have to be taken into account if there were reasons to believe that the chemical proportion of the displaced atoms would be appreciably different from the composition of the alloy. In our case we are dealing with copper and nickel atoms which are similar in size, mass, and atomic number so that one may assume similar threshold energies for displacement E_d, similar kinetic energies transferred, and similar cross sections for collisions.

The first mechanism, chemical changes, is easily disposed of by observing that the susceptibility changes anneal out completely at higher temperatures. The main argument against interpreting the observed changes of susceptibility on irradiation as a consequence of the presence of stable defects is quantitative. According to the present interpretation of the annealing spectra[25,26] of copper irradiated near 10°K, most of the point defects introduced at these temperatures anneal out below liquid nitrogen temperatures, and the remaining ones form clusters or other configurations which could be stable at temperatures even above room temperature. It seems quite justified to apply the same picture to the copper-nickel alloys, and to conclude that only a very small fraction of the one or so percent of atoms which were displaced during irradiation did not return to normal lattice sites at temperatures up to 300C°. In this connection it is worth mentioning the observations of Hirsch[27] who found that after heating copper for 10 minutes at 120°C quenched-in copper vacancies had completely clustered, creating small voids in the crystal. It appears that it would be necessary to assign to these clusters of interstitials or of vacancies (whether collapsed into dislocation loops or not) most unreasonable paramagnetic properties to account for the observed increase in susceptibility of the order of 30 to 40%.

The final alternative is that the redistribution process is the mechanism responsible for the observed susceptibility increase. A solid solution can deviate from perfect randomness either in the direction of segregation caused by a miscibility gap or towards long-range or short-range order. Since in these alloys the susceptibility is a highly nonlinear function of composition, as shown in Fig. 2—note that in this figure susceptibility is plotted on a logarithmic scale—an increase in nickel concentration in one region, coupled with the corresponding decrease in another, would yield a net increase in the susceptibility. It follows that if upon irradiation an initially more or less random copper-nickel solid solution would tend towards further segregation then its susceptibility would increase. This would be true for real segregation, i.e., presence of a miscibility gap as well as for short-range clustering. For the same reason, the formation of short-range order should lower the susceptibility. It is not possible to predict for certain what would be the result of the formation of long-range order since then the electronic configuration may undergo considerable changes.

It is fairly evident, however, that long-range ordering

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[24] Newkirk, Smoluchowski, Geisler, and Martin, Acta Cryst. **4**, 507 (1951).

[25] Magnuson, Palmer, and Koehler, Phys. Rev. **109**, 1990 (1958).

[26] J. W. Corbett and R. M. Walker, Phys. Rev. **110**, 767 (1958).

[27] P. B. Hirsch (private communication).

does not occur for these alloys, within the range of conventional heat treatments: Kaufmann and Starr[28] attempted to detect the presence of long-range ordering near the Cu_3Ni composition by slowly cooling a 30% nickel sample from 820°C to 220°C over the period of 10 days. Within their experimental accuracy of one percent, they were unable to observe any change in the magnetic susceptibility. Similarly, Coles[29] attempted to detect long-range ordering in the Cu-Ni alloy. After cooling some powder samples of 50:50 composition from 900°C to room temperature in 2 days, he was unable to detect any change in the lattice parameter from x-ray patterns as is usually associated with ordering. The electrical resistivity is also "regular," that is, it shows a maximum near the 50:50 composition instead of a sharp local minimum which could be interpreted as evidence of order.

In contrast, there has been some recent work that does indicate the existence of a miscibility gap, or at least of a tendency toward segregation in the copper-nickel alloys. If an alloy system has a miscibility gap then the enthalpy of a perfect mechanical mixture is greater than enthalpy of the system separated into, say, regions of two different compositions. In copper-nickel, where the atoms are so similar, the enthalpy difference associated with the miscibility gap would be necessarily small. At least two different workers have recently obtained positive heats of formation for the copper-nickel system, indicating a miscibility gap. Leach[30] measured the difference between the heats of formation of alloys and the heats of a purely mechanical mixture for a series of copper-nickel alloys ranging up to 50% nickel. He obtained small positive values that increased to about 900 cal/mole at 50% nickel, corresponding to a critical temperature of about 450°K. Agreement was obtained with some values obtained from electrochemical methods. Oriani[31] has recently measured the heats of formation for a series of eleven copper-nickel alloys prepared from solid components at 640°C, ranging from 3 to 93% nickel. He obtained small positive heats of mixing for all of the alloys with a maximum of about 400 cal/mole near 50% nickel, which is appreciably lower than Leach's value. What is important for our purposes is that both authors obtained positive heats of mixing. Meijering *et al.*[32] have made a careful study of the copper-nickel-chromium system. They have found that the addition of as little as 0.7% chromium to copper-nickel alloys, with up to 35% nickel, causes a miscibility gap to appear. This indicates that the copper-nickel system is very close to having a miscibility gap, if it indeed does not have one. From the tie-line directions in the copper-nickel-chromium system, Meijering[33] deduced that the miscibility gap would have a maximum at approximately 450°K, or maybe nearer to room temperature, since at 450°K the jump frequency of the atoms is still about once a day while at room temperature it is effectively nil. A comparison with Au-Pt or Au-Ni systems shows that a critical miscibility temperature near 400°K is compatible with a segregation into 30% and 70% rich alloys near 250°K, as assumed in an illustrative estimate above. It should be pointed out here that the atomic size effect which causes short-range order above the miscibility gap in the Au-Ni system probably does not exist in the Cu-Ni system.

Belov and Goriaga[34,35] have performed measurements of the saturation magnetization of a series of copper-nickel alloys that also indicate deviations from randomness in the alloy system. They investigated the characteristic "tail" in the temperature plot observed near the Curie temperature and found that annealing at successively higher temperatures caused the tail to diminish. This is easily explained if one assumes that the alloy had nonrandom fluctuations in composition before the high-temperature annealing. This would cause the Curie transition to be spread over a small temperature region rather than to occur at a distinct temperature. The high annealing temperatures would return the system to a more random state than the actual state at room temperature; the average composition would then be better defined and the ferromagnetic transition would occur more abruptly. Additional, though much less direct, indication of clustering in the copper-nickel systems may be the fact that these alloys show a very strong solution hardening.[36] This may be related to an increase of the Suzuki effect, i.e., the pinning down of dissociated dislocations by the occurrence of larger composition fluctuations than in a random alloy.[37] Of course, as pointed out by Fisher,[38] short-range order would also add to the hardening. Further evidence for clustering are the results of Köster and Schule,[39] who measured the electrical resistance and the Hall constants for a series of alloys containing up to 45% nickel and found a change of state occurring below 650°C, accompanied by an increase in conductivity and a decrease in the Hall constant. From the behavior of the Hall constant, they concluded that clustering was occurring. Cold working further increased the effect, and aging at elevated temperatures returned the conductivity and Hall constants to their former values characteristic of the statistically disordered solid solution.

[28] A. R. Kaufmann and C. Starr, Phys. Rev. **63**, 445 (1943).
[29] B. R. Coles, J. Inst. Metals **84**, 346 (1956).
[30] J. S. Ll. Leach, National Physical Laboratory Symposium, June, 1958 (to be published).
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[35] K. P. Belov and A. N. Goriaga, Izvest. Akad. Nauk S.S.S.R. Ser. Fiz. **21**, 1038 (1957).
[36] E. Osswald, Z. Physik **83**, 55 (1933).
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[38] J. C. Fisher, Acta Met. **2**, 9 (1954).
[39] W. Köster and W. Schule, Z. Metallk. **48**, 592 (1957).

The interpretation of the observed paramagnetism and of its change with irradiation is thus only possible if we conclude that the alloys tend to be not random at low temperatures and that irradiation accelerates diffusion near room temperature to such an extent that the alloys approach nearer to the state of real equilibrium than they are able to do during a normal cooling process. This formation of more nickel-rich clusters leads then to an increase in superparamagnetism. It is clear that this effect increases with nickel content and reaches a maximum near the 50:50 composition and that it anneals out at higher temperatures.

An exact quantitative evaluation of the above model, in terms of irradiation effects, is difficult because neither the true equilibrium diagram nor the state of the alloys before or after irradiation is well known. An approximate estimate, however, is possible. First one has to inquire into the degree of acceleration of diffusion during irradiation. The best way to do so is to make a comparison with alpha copper-zinc alloys for which the amount of enhancement of diffusion has been measured, in the same reactor, by Dienes and Damask.[40] This is a reasonable procedure since the diffusivity in these alloys, as well as in pure copper and in copper-nickel alloys up to about 50% nickel, is about the same. It appears that irradiation in the Brookhaven National Laboratory reactor accelerates the diffusivity at 80°C by a factor of about 10^5, increasing it from 3×10^{-23} cm^2 sec^{-1} to 3×10^{-18} cm^2 sec^{-1}. This corresponds to an "effective temperature" about 100°C higher than the ambient temperature, and it follows that the mean path of an atom during the time of irradiation of about 40 days is about 300 A instead of 1 A. On the other hand, the mean distance between the minimum clusters which are necessary to account for the observed susceptibility, as indicated above, is of the order of 50 to 100 A. Thus the irradiation provides ample mobility to enhance segregation.

The next question to consider is whether the increase of susceptibility by 30 to 40% upon irradiation is reasonable, that is, whether the dependence of susceptibility on composition is sufficiently nonlinear. It appears that a "best fit" curve gives an increase in susceptibility by a factor of 4 when the nickel content increases from 45 to 48% at 64°K. Thus only a few percent difference in the cluster distribution may easily account for the observed large changes. It would be very interesting to see whether irradiation would affect the temperature coefficient of resistivity of these alloys. In normally prepared alloys, near room temperature, this coefficient can be well accounted for by considering only random concentration fluctuations.[21] Also a change in the saturation magnetization and Curie temperature should be observable.

The final point is the return to a normal, nearly random, distribution at about 300°C. This anneal, which lasts for 50 hours, produces a mean diffusion path of the atoms about 700 A. This is just the right order of magnitude to reverse the segregation produced by the 300 A mean diffusion path during bombardment.

It appears that while a detailed quantitative picture of the statistical nature of the copper-nickel alloys and their paramagnetic properties is still to be worked out its main characteristic, that is, tendency to segregation and superparamagnetism, accounts well for the observed facts.

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[40] G. J. Dienes and A. C. Damask, J. Appl. Phys. **29**, 1713 (1958). Dr. Dienes informs us that his and our irradiations were comparable to somewhat better than a factor of two. This is amply sufficient for our purposes.