The Paramagnetic Susceptibility of Copper-Nickel and Zinc-Nickel Alloys

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Alloys of nickel were prepared with 0 to 60 percent copper or 0 to 30 percent zinc. Their susceptibilities above their Curie temperatures were measured as a function of the temperatures using a Weiss-Foëx magnetic balance at a field of 11,000. Plots of $1/\chi$ against T showed that the Curie-Weiss law holds only in restricted ranges of temperature, the curve becoming concave towards the T axis at high temperatures, especially for the alloys of low nickel content. The susceptibility at a given temperature decreases less rapidly than linearly with percent copper or zinc added. These results are discussed from the points of view of the Heisenberg and the Bloch models.

HE theory of the strong paramagnetism of the ferromagnetic metals and alloys above their Curie points is still in an unsatisfactory state. In general these substances have a region some distance above their Curie points in which the reciprocal of the susceptibility, $1/\chi$, is a linear function of $(T-\theta_p)$, where θ_p is the paramagnetic Curie temperature, while in the region immediately above the Curie point there is a strong curvature. The molecular field theory of Pierre Weiss explains this linearity on a phenomenological basis by the assumption of a "molecular field" in addition to the externally applied field. The attempts to place the molecular field on a theoretical basis were unsatisfactory until Heisenberg showed that the exchange force between the electronic spins in an incomplete inner shell, such as the 3d electrons of nickel, would introduce just such a term. Numerous calculations based on the Heisenberg model have proved the difficulty of determining the actual value of this term. Opechowski1 has carried out a series development, which incorporates preceding results of Heisenberg, and which leads to contradictory results with successive approximations, showing that the convergence is too slow for this method to be reliable. P. R. Weiss and J. H. Van Vleck² applied the Bethe-Peierls method devised for order-disorder transitions. From their calculations a nearly linear relation is found to exist between $1/\chi$ and T over some ranges of temperature but this linearity is accidental and of limited range.

All calculations based on the Heisenberg model are necessarily approximations. This is due to the nature of the model itself which assumes that the electrons responsible for the ferromagnetism are permanently attached to their atoms, thus neglecting any transfer of electrons from atom to atom. Stoner,3 in the alternative method of attack, has used the Bloch modal and treats the 3d as well as the 4s electrons in nickel, for example, as collective electrons, belonging to the metal as a whole. Similarly Mott⁴ has explained the ferromagnetic saturation moment of nickel (0.6 Bohr magneton) by assuming that the 4s energy band is so broadened that it overlaps the 3d band, and in consequence the outer ten electrons in nickel are divided between the 3dand the 4s bands in such a way that on the average there is 0.6 electron per atom in the 4s band and 0.6 electron per atom missing from the 3d band. The ferromagnetic moment below the Curie point and the paramagnetic moment above it are then due to the holes in the 3d band; the 4s electrons cannot contribute magnetic moment because of the great width of the band. Mott adds to this a neat explanation of the change of Curie point and of atomic moment of nickel when alloyed with another metal, such as copper or zinc, which has its 3d shell full and one or two 4s electrons besides. The 3d band is much narrower than the 4s band and thus the density of

^{*} This work was done during a leave of absence from Vassar College as Faculty Fellow, 1937–8. ¹W. Opechowski, Physica 4, 181 (1937).

² P. R. Weiss and J. H. Van Vleck, Phys. Rev. 55, 673 (1939).

³ E. C. Stoner, Magnetism and Matter (Methuen and Company, London, 1934), p. 431.

⁴ N. F. Mott and H. Jones, *The Theory of the Properties of Metal and Alloys* (Oxford University Press, 1936), p. 192.

energy states is much greater. It follows that, on the formation of allovs of nickel, the 4s electrons supplied by copper or zinc will tend to fall into the holes in the 3d band of the alloy until the 3d band is full. This will occur at 60 percent copper or 30 percent zinc. This theory is supported by the ferromagnetic properties of these alloys. Sadron⁵ has shown, if some extrapolation is allowed, that the saturation moment per nickel atom and likewise the Curie temperature decrease in proportion to the copper or zinc added, reaching zero at 60 percent copper or 30 percent zinc. Later we shall see that this support is not so complete as is usually supposed.

The paramagnetic susceptibility above the Curie point also must depend upon the distribution of electrons between 3d and 4s states. Stoner⁶ has carried out this analysis. He finds the observed curvature in the $1/\chi - T$ curve directly above the Curie point consistent with this theory. A linear relation holds at high temperatures because the energy changes fixed by the band structure are relatively less important. Deviations from the Curie-Weiss law in this region may still be explained by a change in the band form or in the number of electrons in the band.

Presumably the actual explanation is somewhere between these two extreme hypotheses and it is accordingly more difficult to formulate. It may be argued that the Heisenberg model is better than the Bloch model in nickel. The reason is that the 3d electrons, which alone are responsible for ferromagnetism in nickel, are rather firmly attached to their atoms. The fact that nickel has an atomic saturation moment of 0.6 Bohr magneton may mean that 60 percent of the nickel atoms are momentarily in the configuration $3d^{9}4s$ and 40 percent in $3d^{10}$. In the alloy there may be a redistribution of the nickel atoms between these configurations. Analyses so far completed fail to include properly fluctuations of atoms between possible configurations. Since the calculations based on the Heisenberg model necessarily neglect the energy associated with the transfer of electrons, results derived from this model may be expected to be in error. The calculated susceptibility will probably be too high.

Another possible error in the results calculated from either model may be attributed to the neglect of the influence of the orbital motion of electrons upon the magnetic susceptibility. In all known cases except that of pyrrhotite the orbital momentum must be nearly quenched at room temperature because the gyromagnetic ratio is almost 2, which would be the value for the electron spin alone. The mechanism for the quenching of this orbital momentum is unexplained on the Heisenberg model. It may be possible that at higher temperatures the orbital momentum might make a contribution to the susceptibility. Since the gyromagnetic ratio is nearly the same for the various metals and their alloys the crystalline field is probably unimportant. The Bloch model explains the quenching as a result of the wandering of electrons from atom to atom. It may also be noted that an antiferromagnetic coupling between the orbital angular momenta may be present and cause such a quenching;⁷ this is not considered in any of the theories.8

In view of the theoretical uncertainties reviewed above it seemed worth while to carry out precise measurements on the susceptibilities of nickel-copper and nickel-zinc alloys above their Curie points. Copper forms a complete series of solid solutions with nickel and zinc is also very soluble in nickel, the solubility limit lying at 30 percent. In both cases there is only a small change in the lattice constant.⁹ Copper and zinc immediately succeed nickel in the periodic table. Thus an atom of nickel in either series of alloys is in a situation very similar to that in the pure metal except that each atom of copper has added one extra electron to the alloy and each atom of zinc has added two. With increasing dilution of nickel and greater average separation between nickel atoms both the ferromagnetic coupling between the 3d electronic spins and the antiferromagnetic coupling of their orbital angular momenta should decrease, and temperature changes dependent upon these factors might be especially apparent.

The paramagnetic susceptibility of copper-

⁵ C. Sadron, Ann. de physique 17, 371 (1932).
⁶ E. C. Stoner, Proc. Roy. Soc. A165, 372 (1938).

⁷ A. Sommerfeld and H. A. Bethe, Handbuch der Physik, second edition, Vol. 24, No. 2, p. 613. ⁸ An excellent review of this subject by J. H. Van Vleck

soon to appear in Ann. de l'Institut Henri Poincaré.

⁹ S. Holgersson, Ann. d. Physik **79**, 35 (1926); J. Schramm, Zeits. f. Metallkunde **30**, 122 (1938).

nickel alloys above their Curie points has already been investigated. The most consistent results are those of Alder¹⁰ and Gustafsson.¹¹ Alder measured the values of the susceptibility from -190 °C to 750 °C and found at all temperatures a decrease in susceptibility as the percent of copper increased, with certain unexplained irregularities. Gustafsson repeated this work but did not find the irregularities previously noted. His measurements extended from room temperature to 450°C. In the present investigation this range has been extended to 800°C, and results compared with similar measurements on zinc-nickel alloys. Since this work was undertaken, the magnetic properties of zinc-nickel have been reported by Schramm.¹² Quantitative comparison is difficult because of the form of the published data.

PREPARATION OF ALLOYS

The alloys were prepared from the purest metals obtainable. The base material was Baker's C. P. nickel, purified further by the rotating cathode method of Fink. This material was prepared by Lawrence Ott in 1931 and has been used in other investigations in this laboratory. This was alloyed with Hilger electrolytic copper, 99.995 percent pure, containing oxygen as the chief impurity. The zinc used was prepared for spectrographic analysis by the New Jersey Zinc Co. and was of 99.999 percent purity. The copper alloys were melted in magnesia crucibles under hydrogen at atmospheric pressure, then pounded to hasten homogenizing, and annealed at a temperature of 900°C for a week. It was very important that homogenizing should be complete since even slight segregations of nickel atoms would cause a large error. As the zinc alloys could not be made in an open crucible, owing to the high volatility of zinc, the zinc and nickel were sealed under a pressure of 10^{-5} mm or less in a small tube of fused silica and annealed at a temperature of 1000°C for a week so that the zinc completely diffused through the nickel. It was impossible to melt these alloys under these conditions due to the low softening point of the container. Spectrographic test for silicon gave negative results.

The homogeneity of the 15 percent copper alloy was tested in two ways, magnetically and microscopically. Specimens of the same melt were polished, etched and examined microscopically by Dr. R. M. Brick of the Department of Metallurgy, after two, five, and seven days homogenizing. No inhomogeneity could be detected even in the two-day sample. The abruptness of the transition at the Curie temperature has been shown by Marian¹³ to be a proof of homogeneity. The transition becomes more abrupt as length of time for homogenizing is increased until a limit is reached when most of the change occurs within from 5 to 20° for copper alloys between 0 and 12 percent, 30 to 60° for 12 to 35 percent copper, and over 60° for alloys with more than 35 percent copper. For this 15 percent alloy the corresponding range in the specimen annealed for two days was 35°, for the one annealed for seven days was 15°. Therefore the magnetic method of test was more sensitive than the microscopic and was used subsequently for all alloys with a Curie point above room temperature. In each case it was found that the transition took place within the temperature limits just quoted from Marian.

The mean composition of these alloys reported was determined by chemical analysis. In different parts of the copper-nickel melt the composition as cast differed by as much as 1 percent for the 15 percent alloy and 2 percent for the 60 percent alloy. The zinc-nickel was of much more uniform composition, the greatest deviation being 0.5 percent for the 9 percent alloy.

The 13 percent copper sample of the coppernickel series was supplied by Dr. R. M. Bozorth of the Bell Laboratories. This was synthesized from Mond nickel (0.03 percent Fe) and Hilger spectroscopically pure copper.

MAGNETIC MEASUREMENTS

A Weiss-Foëx translation balance with a large Weiss magnet was used for the magnetic measurements. The furnace used was similar to one described by Foëx and Forrer¹⁴ and the temperatures were measured by a Chromel-alumel thermocouple calibrated by the melting points of Bi and Sn as indicated by the change of sus-

¹⁰ M. Alder, Thèse, Zurich (1916).

 ¹² G. Gustafsson, Ann. d. Physik 28, 121 (1937).
 ¹² J. Schramm, Zeits. f. Metallkunde 30, 327 (1938).

¹⁸ V. Marian, J. de phys. et rad. [7] **8**, 313 (1937). ¹⁴ G. Foëx and R. Forrer, J. de phys. et rad. [6] **7**, 180 (1926).

<i>T</i> (°K)	$\chi imes 10^6$	$1/\chi \times 10^{-4}$	<i>T</i> (°K)	x×10 ⁶	$1/\chi \times 10^{-4}$	<i>T</i> (°K)	$\chi imes 10^6$	$1/\chi \times 10^{-4}$
599 635 695 743 816 879 899 973 995 1071	13.0 percent Cu by we 51.85 36.50 25.01 19.98 15.06 12.63 12.04 10.28 9.75 8.33	ight 1.929 2.740 3.998 5.005 6.640 7.918 8.306 9.728 10.26 12.00	518 550 626 654 660 689 729 766 792 855 882 933 971	$\begin{array}{r} 42.66\\ 31.89\\ 22.62\\ 19.53\\ 17.69\\ 16.22\\ 15.02\\ 13.54\\ 13.36\\ 11.84\\ 10.98\\ 9.47\\ 8.96\\ 8.24\\ 7.71\end{array}$	$\begin{array}{c} 2.344\\ 3.136\\ 4.421\\ 5.120\\ 5.653\\ 6.165\\ 6.658\\ 7.386\\ 7.485\\ 8.446\\ 9.107\\ 10.56\\ 11.16\\ 12.14\\ 12.97\\ \end{array}$	293 346 404 439 446 565 584 654 690 735 749 806 852 911	$\begin{array}{c} 49.6 \ percent Cu \ by \ w \\ 11.78 \\ 8.45 \\ 6.83 \\ 6.26 \\ 6.16 \\ 5.35 \\ 4.71 \\ 4.55 \\ 4.12 \\ 4.03 \\ 3.79 \\ 3.71 \\ 3.53 \\ 3.37 \\ 3.22 \end{array}$	eight 8.489 11.84 14.65 15.96 16.24 18.70 21.24 21.97 24.25 24.83 26.47 26.92 28.32 29.67 31.02
518 563 582 633 680 712 789 833 952 1084	$\begin{array}{c} 225.15\\ 80.64\\ 61.99\\ 36.26\\ 26.77\\ 22.51\\ 16.30\\ 14.30\\ 10.64\\ 8.45\end{array}$	$\begin{array}{r} .4441\\ 1.240\\ 1.613\\ 2.759\\ 3.736\\ 4.442\\ 6.135\\ 6.993\\ 9.398\\ 11.84\end{array}$	475 500 561 573 612 642 693 753 809 876 957	28.7 percent Cu by a 31.58 25.69 17.33 16.46 13.73 12.37 10.77 9.17 8.10 7.07 6.26	veight 3.167 3.893 5.770 6.075 7.283 8.084 9.285 10.91 12.34 14.15 15.98	293 345 396 447 501 563 606 650 703 747 827 897 948	$11.37 \\ 8.10 \\ 6.93 \\ 5.95 \\ 5.18 \\ 4.51 \\ 4.29 \\ 3.97 \\ 3.78 \\ 3.57 \\ 3.31 \\ 3.15 \\ 3.05$	$\begin{array}{r} 8.79\\ 12.34\\ 14.43\\ 16.79\\ 19.32\\ 22.17\\ 23.33\\ 25.21\\ 26.46\\ 27.98\\ 30.21\\ 31.74\\ 32.79\end{array}$
558 575 633 669 721 808 854 913 983 1054	15.0 percent Cu by w 72.63 57.92 32.81 25.98 20.30 14.76 12.87 11.24 9.83 8.77	eight 1.377 1.727 3.048 3.849 4.926 6.775 7.770 8.897 10.17 11.40	429 454 483 534 534 625 668 724 765	52,4639,8929,1420,3415,9413,3511,369,788,87	$\begin{array}{c} 1.906\\ 2.507\\ 3.432\\ 4.916\\ 6.274\\ 7.491\\ 8.803\\ 10.22\\ 11.27\end{array}$	295 341 382 439 480 530 580 627 635 728 810	60.9 percent Cu by u 3.30 3.01 2.78 2.58 2.52 2.43 2.35 2.31 2.30 2.20 2.12	2029 2020
593 600 640 691 741 789 890 939 471	50.65 45.94 33.39 24.57 19.20 15.96 12.08 10.85 22.7 percent Cu by u 81.65	1.974 2.177 2.995 4.070 5.208 6.266 8.278 9.217 reight 1.225	331 380 397 442 489 539 573 609 657 687 751	37.0 percent Cu by 53.30 28.84 25.24 17.97 13.53 10.97 9.82 8.81 7.63 7.13 6 31	weight 1.876 3.467 3.962 5.565 7.391 9.116 10.18 11.36 13.10 14.02 15.85	294 345 399 447 504 557 612 655 709 757 819 857	$\begin{array}{c} 3.27\\ 2.95\\ 2.68\\ 2.58\\ 2.43\\ 2.35\\ 2.27\\ 2.23\\ 2.18\\ 2.13\\ 2.07\\ 2.04\end{array}$	$\begin{array}{c} 30.61\\ 33.92\\ 37.30\\ 38.68\\ 41.07\\ 42.54\\ 44.05\\ 44.82\\ 45.87\\ 47.04\\ 48.40\\ 48.40\\ 48.97\end{array}$
484 487 511 533 547 554 596 602 629 645 701 754	$\begin{array}{c} 69.09\\ 63.22\\ 55.40\\ 48.41\\ 37.96\\ 32.75\\ 32.39\\ 26.01\\ 23.37\\ 23.48\\ 20.53\\ 18.29\\ 14.93\\ 12.79\end{array}$	$\begin{array}{c} 1.447\\ 1.582\\ 1.805\\ 2.066\\ 2.634\\ 3.053\\ 3.087\\ 3.845\\ 4.279\\ 4.259\\ 4.259\\ 4.871\\ 5.467\\ 6.698\\ 7.819\end{array}$	412 483 550 607 641 688 721 775 840 876 941 970	$\begin{array}{c} 21.31\\ 13.80\\ 10.37\\ 8.66\\ 7.97\\ 7.18\\ 6.73\\ 6.08\\ 5.52\\ 5.26\\ 4.87\\ 4.73\end{array}$	$\begin{array}{r} 4.693\\7.246\\9.643\\11.55\\12.54\\13.93\\14.85\\16.44\\18.11\\19.02\\20.54\\21.14\end{array}$	900 976	2.01 1.97	49.85 50.84

TABLE I. Mass susceptibilities of CuNi alloys. The results on two different specimens are given for each alloy.

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<i>T</i> (°K)	$\chi \times 10^{6}$	$1/\chi \times 10^{-4}$	<i>T</i> (°K)	$\chi imes 10^6$	$1/\chi \times 10^{-4}$	T(°K)	$\chi imes 10^{6}$	$1/\chi \times 10^{-4}$
677 709 722 779 816 863 902 926 993	5.1 percent Zn by weight 43.69 33.47 31.42 22.70 19.45 16.27 14.65 13.66 11.70	$\begin{array}{c} 2.289\\ 2.988\\ 3.183\\ 4.405\\ 5.141\\ 6.146\\ 6.826\\ 7.321\\ 8.547\end{array}$	445 487 554 603 646 692 743 806 849 905 935	$\begin{array}{r} 17.0 \ percent \ Zn \ by \\ 26.38 \\ 19.80 \\ 14.51 \\ 12.40 \\ 10.83 \\ 9.75 \\ 8.69 \\ 7.64 \\ 7.16 \\ 6.74 \\ 6.56 \end{array}$	weight 3.791 5.051 6.892 8.065 9.234 10.25 11.50 13.09 13.97 14.83 15.24	293 346 398 443 505 563 594 669 723 848 904 959	$\begin{array}{c} \textbf{26.2 percent Zn b}\\ \textbf{9.09}\\ \textbf{7.54}\\ \textbf{6.53}\\ \textbf{5.96}\\ \textbf{5.28}\\ \textbf{4.85}\\ \textbf{4.65}\\ \textbf{4.65}\\ \textbf{4.26}\\ \textbf{4.06}\\ \textbf{3.72}\\ \textbf{3.59}\\ \textbf{3.51} \end{array}$	y weight 11.00 13.26 15.31 16.79 18.93 20.62 21.52 23.45 24.62 26.87 27.84 28.51
656 690 716 769 790 833 864 890 914 951	51.22 38.63 31.59 23.41 21.53 18.21 16.37 15.06 14.09 12.80	$\begin{array}{c} 1.952\\ 2.589\\ 3.166\\ 4.272\\ 4.645\\ 5.491\\ 6.109\\ 6.640\\ 7.097\\ 7.812\end{array}$	406 423 452 497 558 572 654 688 693	37.65 32.51 25.55 18.74 14.37 13.52 10.47 9.55 9.37	2.656 3.076 3.914 5.336 6.959 7.396 9.551 10.47 10.67	293 347 394 468 518 593 687 739 817 843 911 974	$\begin{array}{c} 9.14\\ 7.49\\ 6.67\\ 5.75\\ 5.23\\ 4.66\\ 4.15\\ 3.97\\ 3.75\\ 3.68\\ 3.54\\ 3.44\end{array}$	$10.93 \\ 13.35 \\ 14.99 \\ 17.39 \\ 19.11 \\ 21.47 \\ 24.09 \\ 25.17 \\ 26.66 \\ 27.18 \\ 28.22 \\ 29.10 \\$
590 626 658 687 749 818 847 855 902 954 957 991 1001	$\begin{array}{r} 9.1 \ percent \ Zn \ by \ weigh \\ 46.68 \\ 32.52 \\ 27.65 \\ 22.29 \\ 18.11 \\ 17.17 \\ 14.06 \\ 12.74 \\ 12.54 \\ 11.27 \\ 10.13 \\ 10.07 \\ 9.51 \\ 9.38 \end{array}$	2.145 3.075 3.617 4.486 5.522 5.824 7.974 8.873 9.872 9.930 10.52 10.66	295 363 419 479 545 600 642 688 742 782 823 885 962	21.2 percent Zn by 32.60 18.88 13.95 11.00 8.79 7.80 7.11 6.59 6.08 5.80 5.55 5.17 4.90	weight 3.067 5.297 7.168 9.091 11.38 12.82 14.07 15.18 16.45 17.25 18.00 19.33 20.41	293 327 371 396 441 502 582 645 698	29.7 percent Zn b 5.22 5.02 4.61 4.36 4.12 3.84 3.55 3.40 3.31	ry weight 19.14 19.92 21.69 22.93 24.24 26.01 28.14 29.38 30.24
518 536 558 570 604 625 650 679 702 729 751 784	$\begin{array}{c} 132.45\\ 92.50\\ 65.27\\ 58.11\\ 39.49\\ 33.11\\ 28.27\\ 23.88\\ 21.23\\ 19.08\\ 17.31\\ 15.61\end{array}$	$\begin{array}{c} 0.7553\\ 1.081\\ 1.532\\ 1.721\\ 2.532\\ 3.020\\ 3.537\\ 4.188\\ 4.710\\ 5.241\\ 5.777\\ 6.406\end{array}$	294 309 312 338 366 514 517 592 683 689 765 832 883 947	$\begin{array}{c} 33.13\\ 27.06\\ 26.48\\ 21.64\\ 18.04\\ 16.28\\ 11.06\\ 9.80\\ 9.60\\ 8.04\\ 6.71\\ 6.72\\ 6.05\\ 5.62\\ 5.32\\ 5.03\end{array}$	$\begin{array}{c} 3.018\\ 3.695\\ 3.776\\ 4.621\\ 5.543\\ 6.143\\ 9.042\\ 10.21\\ 10.42\\ 12.44\\ 14.89\\ 14.88\\ 16.54\\ 17.80\\ 18.81\\ 19.88\\ \end{array}$	293 345 449 510 554 610 664 745 835 900 957	5.14 4.66 3.97 3.69 3.54 3.25 3.11 2.99 2.91 2.86	$19.44 \\ 21.45 \\ 25.18 \\ 27.06 \\ 28.26 \\ 29.21 \\ 30.77 \\ 32.18 \\ 33.44 \\ 34.38 \\ 34.94$

TABLE II. Mass susceptibilities of ZnNi alloys. The results on two different specimens are given for each alloy.

ceptibility. As only relative susceptibilities were obtained by this method, absolute values were found by comparison with a standard of pure gold of known mass susceptibility (0.145 ± 0.001) $\times10^{-6}$.

sealed into silica tubes under a pressure of 10^{-5} mm to prevent change of composition due to diffusion and oxidation. After a measurement at a high temperature a repetition of one at a low temperature was made as a test for any permanent change which might have occurred in

For these measurements the specimens were



FIG. 1. Reciprocals of mass susceptibilities of CuNi alloys plotted against the temperatures for various percents of copper.

the specimen. When a run had been completed the container was cracked open, the specimen removed, and the susceptibility of the silica measured separately.

To prove the absence of ferromagnetic impurity (e.g., undissolved nickel) the susceptibility was measured at several values of the magnetic field between 3000 and 15,000, at both room and higher temperatures, and in no case was there a deviation from proportionality between susceptibility and field. Subsequently measurements of susceptibility *versus* temperature were taken at a fixed field of 11,350.

DISCUSSION OF RESULTS

Tables I and II give the data, T and χ , and the calculated values of $1/\chi$ for the copper and zinc alloys, respectively. These results are presented graphically in Figs. 1–4, a separate curve being drawn for each specimen in Figs. 1 and 2. Gustafsson's values for copper-nickel at the corresponding temperatures are plotted for comparison in Fig. 3; for each temperature his points (crosses) lie slightly higher than the curves obtained here.

These results show, in the first place, that the Curie-Weiss law holds only within restricted ranges of temperature. When measurements could be obtained in the neighborhood of the Curie point, the curves become convex towards the T axis as is usual. At high temperatures, on the other hand, the curves become concave towards the T axis, especially for the alloys of low nickel content. The second important result is that the susceptibility at a given temperature decreases less rapidly than linearly with the addition of copper or zinc. Thus extrapolation to zero moment at 60 percent copper or 30 percent zinc is not justified. If the percent copper or zinc were plotted against average moment per nickel atom instead of moment per gram of alloy the general shape of the curves would be the same although the absolute value of the slope would decrease more rapidly with increase of copper or zinc.

In the preceding discussion of the $1/\chi - T$ curves based on the Bloch model it was mentioned that the Curie-Weiss law ought to hold best at high temperatures. Thus the curvature found for these alloys at high temperatures is not predicted by this theory. One cause for a

deviation from the Curie-Weiss law could be a change in the form of the energy band at the high temperatures, due to a change in the lattice constant. When the temperature is raised and the lattice expands the band becomes narrower, causing an increase in susceptibility. The coefficient of thermal expansion of the copper-nickel alloys, at least, is known to obey the law of mixtures, increasing from the value for nickel proportionately to the percent copper added. Thus this effect would be greater in the alloys of high copper content. This is just what is found: the susceptibility at high temperatures is larger than that predicted by the Curie-Weiss law, particularly for alloys high in copper or zinc. It may be doubted, however, in view of the small total change in lattice constant, whether any such secondary effect could be important.

A second possible cause for a deviation from the theoretical curve would be a change in the number of electrons in the band. It may be possible that at higher temperatures and lower nickel contents the 4s electrons do not so readily



FIG. 2. Reciprocals of mass susceptibilities of ZnNi alloys plotted against the temperatures for various percents of zinc.



FIG. 3. Mass susceptibilities *versus* percent copper by weight for various temperatures. Gustafsson's values are indicated by crosses.

fall into the holes in the 3d band, with the result that in such cases the susceptibility is abnormally increased.

The second experimental result, that the susceptibility drops more slowly than in proportion to the copper or zinc content, contradicts the predictions of the Curie-Weiss law, $\chi = C/(T - \theta_p)$. By this theory in its simple form both C and θ_p are proportional to the number of paramagnetic atoms. Thus the susceptibility should decrease more rather than less rapidly than is required by a linear relation between χ and percent composition. This suggests again that the 4s electrons do not inevitably fill the empty spaces in the 3dshell, particularly at high copper and zinc content. This is difficult to reconcile with the Bloch model without special modifications. In fact the exchange interaction between the electronic spins should decrease with increased separation of the nickel atoms, resulting in a

decreased value of θ and therefore a decreased susceptibility.

As yet the Heisenberg model also has not been sufficiently developed to explain either of these results satisfactorily. It should be emphasized that a linear relation between $1/\chi$ and T is not necessarily predicted by this theory. A small excess susceptibility at the high temperatures could be explained by a redistribution of the nickel atoms from d^{10} to d^9 configurations. This is, of course, comparable to the scattering of an electron from a d to an s band in the Bloch model, and is equally incalculable. Anomalous increase of susceptibility at high temperatures might also be qualitatively explained by unquenching of orbital momenta.

No predictions have been made from this point of view about the variation of the susceptibility with the percent copper or zinc added. If only the nickel atoms contribute magnetic moment, these results indicate that there may be a redistribution of the nickel atoms between the d^{10} and d^{9} states with alloying. If the orbital moment is quenched due to an antiferromagnetic coupling this would decrease as the average distance between the nickel atoms increased. An added susceptibility would then result from the magnetic contribution of the orbital momenta in the alloys of low nickel content. On the other hand, as mentioned before, the ferromagnetic coupling of the electronic spins would also decrease with increased separation of the nickel atoms, causing a decrease in θ and with it a decrease in the susceptibility. Any change in the antiferromagnetic coupling or in the spin-orbit coupling would cause the gyromagnetic ratio to differ from 2. Sucksmith¹⁵ found a g value of 1.9 at room temperature for copper-nickel alloys with Curie points around -10° C, which shows that the influence of the orbital momenta is not important just above the Curie point. Similar measurements on alloys with lower Curie points would be very illuminating as the orbital momenta are more apt to be liberated at temperatures well above the Curie point.

A comparison of the susceptibilities for the two sets of specimens shows that an alloy with a

¹⁵ W. Sucksmith, Helv. Phys. Acta 8, 205 (1935).

certain percent zinc corresponds most closely to the alloy with twice that percent copper. The ratio of the susceptibility of the zinc alloy to that of the corresponding copper alloy is always greater than unity but is never greater than 1.5. In general, it is higher for the alloys of low percent nickel. In other words, any factor which causes an increase in susceptibility is stronger in zinc alloys than in copper alloys having the same number of excess electrons.

No corrections for the diamagnetism of the core or for temperature independent paramagnetism were made. The atomic moment was not calculated because of the inadequacies of the Curie-Weiss law. These results agree with Gustafsson's in showing no sudden changes of slope such as were found by Alder.

The ferromagnetic Curie point was above room temperature in a few cases so that it could be measured and compared with the paramagnetic Curie point.¹⁶ For the 15 percent copper alloy the temperature of the ferromagnetic Curie point was measured for the sample annealed for two days and for one annealed for five days. The transition from ferromagnetic to paramagnetic state was not only more gradual for the two-day sample, as already mentioned, but the value of θ_f at the point of inflection was higher for the two-day sample. The value of θ_p was the same within experimental error.

In conclusion it should be repeated that the explanation of these results is necessarily incomplete because neither the Bloch nor the Heisen-

	θ_{f}	θ_p		θſ	θ_p
¹⁶ 13 percent Cu	488°K	508°K	5 percent Zn	532	560
15 percent Cu	474	500	9 percent Zn	457	487
23 percent Cu	394	420			
29 percent Cu	351	370			



FIG. 4. Mass susceptibilities versus percent zinc by weight for various temperatures.

berg model adequately describes the state of the alloy, and because many factors have had to be neglected in the calculations.

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