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The Effect of Cold Working on the Magnetic Properties of Pure Metals

JAMES REEKIE
Department of Physics, University of Toronto, Canada

AND

T. S. HUTCHISON
Department of Physics, University of St. Andrews, Scotland

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Experiments with aluminum and copper of the highest purity obtainable show that the magnetic susceptibilities of these metals are appreciably altered by cold working. The paramagnetic susceptibility of aluminum is decreased by an amount reaching approximately 15 percent of the original value, and the diamagnetic susceptibility of copper is also, numerically, decreased by nearly the same amount. This strain sensitivity of susceptibility cannot be accounted for by the presence of ferromagnetic impurities, but appears to be related to certain metallurgical changes which occur on cold working. From a consideration of the magnitude of $\Delta\chi$ for different degrees of cold work and the phenomenon of "magnetic self-recovery" (observed in copper but not in aluminum), it is concluded that the combined effects of lattice distortion and fragmentation probably give rise to the observed changes in magnetic susceptibility.

An explanation of the results is suggested in terms of trapping of the "free" electrons in the cold-worked metal at points of considerable internal strain, and a simple application of Stoner's theory of the susceptibility of free electrons appears capable of giving a qualitative indication of why cold working should cause a change of χ towards *increased* paramagnetism in copper but towards *decreased* paramagnetism in aluminum.

I. INTRODUCTION

IT is well known that certain physical properties of metals are markedly affected by the mechanical treatment to which they have been subjected. This is especially significant in the case of the mechanical properties themselves, and while the work-hardening of annealed pure metal is perhaps the commonest observation of this type, changes in electrical resistivity, magnetic properties, and certain thermal properties, as well as in the crystal texture of the metal itself due to cold working, have been recorded by many observers. This present paper is concerned with the effect of cold working on the magnetic properties of pure copper and aluminum; it forms part of a systematic investigation of a number of pure metals and of certain metals with small, known, percentages of iron as impurity. The purpose of the work has been to try to correlate the observed magnetic changes with certain metallurgical changes which are known to occur during cold working, with the ultimate aim of arriving at some understanding of the actual mechanism whereby cold working can bring about such changes.

II. EVIDENCE FOR STRAIN SENSITIVITY OF MAGNETIC SUSCEPTIBILITY

The fact that the magnetic susceptibility of a metal depends in part on its mechanical condition has been known for a long time.[1] For instance, it was found by Bitter,[2] and also by Lowance and Constant,[3] that a relatively small degree of cold working reduced the numerical values of the susceptibilities of the diamagnetic metals, copper, silver, and bismuth, while the paramagnetic susceptibility of platinum was increased. It will be noted that in each case this change of susceptibility could be regarded as a change in the direction of increased paramagnetism. Change towards paramagnetism is not the invariable result however; paramagnetic aluminum, for instance, shows a *reduction* of susceptibility on cold working.

Although the change of magnetic susceptibility with cold work is a well established fact, the reasons for this change are still by no means clear. Attempts have been made to attribute

[1] See, for example, K. Honda and Y. Shimizu, Nature **126**, 990 (1930); Y. Shimizu, Sci. Rep. Tohoku Univ. **20**, 460 (1931).
[2] F. Bitter, Phys. Rev. **36**, 978 (1930).
[3] F. E. Lowance and F. W. Constant, Phys. Rev. **38**, 1547 (1931).

changes in magnetic properties induced by cold work in supposedly pure metals to the presence of minute amounts of ferrous impurity. This impurity is assumed to be in a non-magnetic state in the annealed metal, but to precipitate out in ferromagnetic form on cold working. The very careful work of Kussmann and Seemann,[4] in which susceptibility was measured as a function of the applied magnetic field in the case of cold worked metals containing traces of iron as impurity, lent support to this view.

In the case of a diamagnetic substance, such as copper, precipitation of an iron impurity in ferromagnetic form would result in a change in the observed susceptibility towards increased paramagnetism. If the impurity were present in sufficient quantity the substance might well appear to be paramagnetic, as has often been reported in the case of copper.[2,5] In such a case there would be, however, a marked variation of apparent susceptibility with magnetic field.

Furthermore, in a paramagnetic metal precipitation of ferromagnetic impurity by cold working should result not only in a marked dependence of susceptibility on field strength, but also in an *increase* in apparent paramagnetic susceptibility. We have found, on the contrary, that the paramagnetic susceptibility of aluminum *decreases* considerably on cold working.

In the present work the susceptibility was always measured as a function of field strength, on both annealed and cold-worked specimens, generally in fields up to about 15,000 oersted. The high purity of the metals used, together with the absence of any appreciable field dependence of susceptibility in either the annealed or cold worked states, leads us to conclude that the changes in susceptibility observed require some considerably more fundamental explanation than the presence of impurities. We believe that the magnetic changes can be linked up fairly satisfactorily with certain metallurgical changes which occur as a result of cold working, and an explanation along these lines is attempted. In addition, some degree of correlation with Stoner's theory of free electron susceptibility[6] can be introduced, and the recently reported "self-recovery" effects noted in x-ray observations on cold-worked copper[7] are almost certainly associated with the "magnetic self-recovery" which we recently described as occurring in cold-worked copper.[8]

III. PREPARATION OF SPECIMENS

A. Metals Used

This work has been carried out with copper and aluminum of the highest purity, electrolytically refined "H.S." brand, provided by Johnson, Matthey, and Company, Ltd. of London, England. The metal was obtained in the form of rods 15 cm long and 5 or 6 mm in diameter. The iron content of the materials was stated to be, by chemical analysis, "certainly less than 0.0005 percent," and "not detectable by spectroscopic analysis." From the magnetic measurements it is clear that the iron content must have been much less than the upper limit quoted in the chemical analysis.

B. Heat Treatment

The effect of heat treatment on the magnetic properties of metals containing ferrous impurity can be very considerable, and for this reason the heat treatment used during the present work has followed a relatively simple but standardized procedure.

In the case of aluminum, annealing was always carried out by heating the rod of metal in an atmosphere of hydrogen at a temperature of 500°C for approximately two hours. Annealing of the copper rods was carried out by heating in hydrogen at a temperature of 950°C to 1000°C for a period of approximately ten hours.

Subsequent cooling of the specimens was dependent on the particular investigation being made. If the specimen was required in the "quenched" condition, it was transferred rapidly from the high temperature furnace into water at room temperature; the hydrogen atmosphere was maintained surrounding the metal until it

[4] A. Kussmann and H. J. Seemann, Naturwiss. **19**, 309 (1931); Zeits. f. Physik **77**, 567 (1932). See also, C. S. Smith, Phys. Rev. **57**, 337 (1940).
[5] Y. Shimizu, Sci. Rep. Tohoku Univ. **22**, 915 (1933).
[6] E. C. Stoner, Proc. Roy. Soc. **A152**, 672 (1935).
[7] H. Megaw, H. Lipson, and A. R. Stokes, Nature **154**, 145 (1944); M. Cook and T. Ll. Richards, J. Inst. Metals **70**, 159 (1944); H. Megaw and A. R. Stokes, *ibid.* **71**, 279 (1945); L. L. van Reijen, Nature **157**, 371 (1946); J. L. Miller, L. C. Bannister, and R. M. Hinde, *ibid.* **158**, 705 (1946); W. G. Burgers, *ibid.* **159**, 203 (1947).
[8] J. Reekie and T. S. Hutchison, Nature **157**, 807 (1946).

entered the water. "Slow cooling" was carried out by allowing the metal to cool from its annealing temperature down to room temperature over a period of about eight hours, both for the copper and aluminum, again maintaining a hydrogen atmosphere during the whole period of cooling.

C. Cold Working

Throughout the observations described in the present paper, cold working of the materials has been carried out by drawing the previously annealed rods through hardened steel dies at a uniform rate until the required degree of reduction in diameter was achieved. The direction of draw was always maintained the same, for every specimen, and particular care was taken to avoid any contamination of the pure metals during the drawing processes.[9] The results indicate that no measurable contamination occurred.

No very satisfactory criterion for the specification of the degree of cold working in any simple manner has yet been formulated, though possibly the most logical method would be to determine the amount of stored energy in the cold-worked material, as in the experiments of Taylor and Quinney.[10] However, it has become customary to adopt as an arbitrary measure of cold work the degree of reduction in cross-sectional area of the material, and this definition is adopted in the present paper.

IV. EXPERIMENTAL PROCEDURE

The susceptibility was determined in all cases by the Gouy method, using specimens approximately 12 cm long and of various diameters from about 5 mm down to about 2 mm. In this method it is necessary to measure the force exerted on a specimen of known dimensions when acted on by a magnetic field, and for this purpose we used a small electrodynamic balance and a conventional type of electromagnet. An account of the construction and use of the balance itself has been given elsewhere, and the experimental procedure has been described in previous publications,[11,12] to which reference should be made for details.

V. MEASUREMENT OF MAGNETIC SUSCEPTIBILITY

If a rod of material of uniform cross section α and magnetic susceptibility per unit volume k is suspended so that one end is in a uniform field H and the other in a field H_0, the length of the rod being perpendicular to these fields, then a force is exerted on the material in a direction at right angles to the magnetic field H. The magnitude of this force is given by

$$F=\tfrac{1}{2}(k-k')\alpha(H^2-H_0^2) \text{ dynes,} \qquad (1)$$

where k' is the volume susceptibility of the medium surrounding the rod.

This, as is well known, forms the basis of the Gouy method of measuring magnetic susceptibilities. In the present work the specimen was surrounded by hydrogen gas at a few cm pressure so that no appreciable error was introduced by neglecting k', and the expression for the force can then be written as

$$F=\tfrac{1}{2}m\chi(H^2-H_0^2)/l. \qquad (2)$$

Here m and l are, respectively, the mass and length of the rod, and χ is the susceptibility per gram, i.e., the mass susceptibility.

From this expression it can be seen that if χ is a constant independent of the field, then the force exerted on the specimen should be strictly proportional to the quantity $(H^2-H_0^2)$. This, as has already been indicated, forms a sensitive test for the presence of ferromagnetic impurities, because, in the case of a ferrrous material, χ is a function of the field strength itself, so that F is no longer a linear function of $(H^2-H_0^2)$. However, in such a case, values of χ for the pure material can still be obtained by several well-known methods.[13]

In no instance during the present work could it be said that any definite indication of ferromagnetism was observed, either with the metals in the annealed state or after considerable

[9] See, for example, Philips Technical Review **8**, 315 (1946).

[10] G. I. Taylor and H. Quinney, Proc. Roy. Soc. **A163**, 157 (1937).

[11] J. Reekie, Proc. Roy. Soc. **A173**, 367 (1939).

[12] T. S. Hutchison and J. Reekie, J. Sci. Inst. **23**, 209 (1946).

[13] See, for example, L. F. Bates, *Modern Magnetism* (Cambridge University Press, Teddington, England, 1939), p. 116.

degrees of cold working. In all cases the force exerted on the specimen was found to be, very closely, a linear function of $(H^2-H_0^2)$ over the whole range of fields used, any initial curvature not being outside the experimental error. The fact that χ, as obtained from Eq. (2), shows no evidence of field dependence in any of these measurements must be taken as strong evidence that ferromagnetic impurities play no part in the effects to be described later.

VI. CHANGE OF MAGNETIC SUSCEPTIBILITY ON COLD WORKING

Using a number of specimens annealed in the manner previously described and measured as outlined above, we have found the average value of the susceptibility of pure copper to be -0.085×10^{-6} c.g.s. units per gram at a temperature of about 290°K. Taking into account all sources of error this value is considered to be correct to within about 3 percent.

If any specimen is cold-worked by drawing, the susceptibility is found to decrease (numerically), even for small degrees of cold work. For example, a four percent reduction in area of the specimen reduces the value of mass susceptibility to -0.079×10^{-6}, while at 20 percent reduction in area the susceptibility becomes -0.072×10^{-6}, both values being measured at room temperature. This change is in the direction of increased paramagnetism and, as has been pointed out, is not inconsistent with the possibility of ferromagnetic impurity being precipitated as a result of the cold working.

Equally marked changes are observed in the susceptibility of cold-worked aluminum, but in this case the paramagnetic susceptibility *decreases* with cold working. For example, the annealed metal gives an average value for χ at room temperature of $+0.62\times10^{-6}$ c.g.s. units per gram; seven percent cold working reduces this to 0.60×10^{-6}, while the same specimen cold-worked to 30 percent reduction of area has a susceptibility of 0.54×10^{-6}. It does not seem possible to explain a *decrease* in paramagnetic susceptibility as caused by precipitation of ferrous impurity.

Table I gives the measured values of mass susceptibility of aluminum and copper for a number of different degrees of cold working. These figures refer to one particular specimen of each metal, subjected to successively increasing degrees of cold work. Check measurements on other specimens cold-worked to similar degrees and then re-annealed showed that in all cases annealing caused the susceptibility to revert to its original value, within the limits of accuracy of the measurements. For reasons which will be apparent later, all susceptibility measurements were carried out one hour after the cold working of the metal had taken place.

TABLE I. Mass susceptibility for different degrees of cold working.

Aluminum Cold work: percent reduction of area	$\chi\times10^{+6}$	Copper Cold work: percent reduction of area	$\chi\times10^{+6}$
Annealed	$+0.62_3$	Annealed	-0.085
14.4	0.60_4	2	0.084
18	0.58_6	4	0.079
19	0.56_8	6	0.075
22.6	0.55_2	20	0.073
23.4	0.54_4	34	0.072
32	0.53_8	43	0.074
42	0.53_3	50	0.073
55	$+0.52_8$	59	0.077
		65	0.076
		69	0.076_5
		73	-0.080_5

At this stage, one feature of these results calls for comment. It will be evident in the case of copper that when cold working is in excess of about 45 percent reduction in area the measured susceptibility begins to *increase* (numerically) again. This point appears to be of considerable significance in the explanation of the results and will be discussed later.

The comparative behavior of aluminum and copper is illustrated in Fig. 1, where the percentage change of susceptibility is shown as a function of the degree of cold work. The numerical increase of χ towards its "annealed" value for cold working in excess of 45 percent in the case of copper is also clearly shown in this diagram. (χ_0 represents the susceptibility of the annealed metal, and $\Delta\chi$ the difference between the cold worked and annealed values.)

VII. MAGNETIC SELF-RECOVERY

A. Rate of Recovery of Different Temperatures

During our first investigations on the effect of cold working on the susceptibility of copper it was noted that the numerical value of the susceptibility of the cold-worked metal appeared to increase slowly with time, all other experimental conditions remaining undisturbed. A more detailed investigation of this effect revealed that a noticeable "magnetic self-recovery" takes place in copper,[8] even at temperatures far below that at which recrystallization can occur. The rate of recovery is, as might be expected, dependent on the temperature and can, in fact, be arrested altogether at sufficiently low temperatures. It is because of this magnetic self-recovery that all susceptibilities quoted in the previous section were measured at a specific time, namely, one hour after cold working.

In carrying out these investigations a previously annealed copper rod was cold worked and then assembled in the balance for measurement. The susceptibility was observed one hour after the cold working had been completed, and thereafter at convenient intervals over periods as long in some cases as 100 hours. During the whole time of the measurements on any single specimen the temperature of the specimen was maintained constant. Cold working was, of course, always carried out at room temperature, and, after assembly in the balance, the specimen taken as rapidly as possible to the temperature at which it was desired to carry out susceptibility measurements.

As typical of the recovery effects observed,

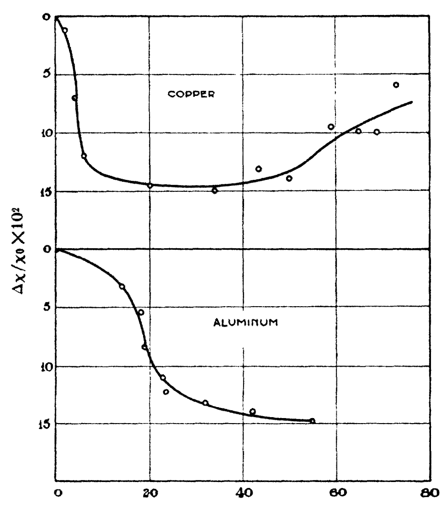

FIG. 1. Percentage change in susceptibility at room temperature as a function of cold working. For copper $\chi_0 = -0.085 \times 10^{-6}$. For aluminum $\chi_0 = +0.62 \times 10^{-6}$.

Fig. 2 shows the change in the measured value of susceptibility as a function of time after cold working, for specimens maintained at three different temperatures. In the diagram $\Delta\chi$ is the actual change in susceptibility and χ the susceptibility of the particular specimen as measured one hour after cold working. During each set of measurements the specimen and the balance remained undisturbed, so that the *relative* accuracy of the points on any particular curve in Fig. 2 is better than $\frac{1}{2}$ percent.

Several features will be evident at once. In the first place, a considerable "recovery" of the susceptibility towards its "annealed" value takes place at room temperature. This recovery can be accelerated by raising the temperature a relatively small amount, while if the specimen is maintained at the temperature of liquid air no measurable recovery takes place. Furthermore, the recovery observed is at most about six percent of the initial value of χ, so that the "recovered" value of susceptibility is still considerably less than the value for the annealed metal at the same temperature. The recrystallization temperature of copper is about 200°C, so that recovery effects of the magnitude observed here cannot be attributed reasonably to recrystallization, nor could any change of state of ferrous impurity occur at these temperatures. It is suggested that this magnetic self-recovery reflects the self-recovery from lattice distortion which recent x-ray observations have made clear.[7] This suggestion will be elaborated when considering the interpretation of the results.

On carrying out similar measurements with aluminum rods cold-worked to varying degrees, no detectable change of susceptibility was noted, even with observations extending over periods of as much as 70 hours at room temperature. Specimens cold-worked up to 50 percent reduction in area were used in these measurements.

The absence of magnetic self-recovery in aluminum may, at first sight, appear difficult to reconcile with the suggested explanation in the case of copper. This is not so however, because the x-ray work of Wood[14] has shown that aluminum is *spontaneously self-recovering during cold*

[14] W. A. Wood, Proc. Roy. Soc. **A172**, 231 (1939); Proc. Phys. Soc. London **52**, 110 (1940). See also A. Taylor, *Introduction to X-ray Metallography* (Chapman and Hall, Ltd., London, 1945), p. 234.

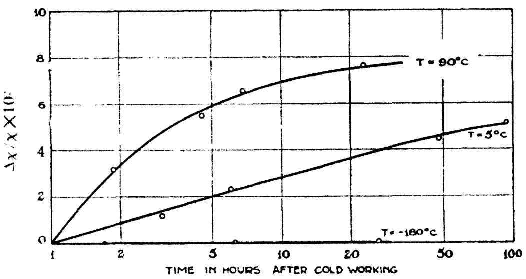

FIG. 2. Magnetic self-recovery of cold-worked copper at various temperatures.

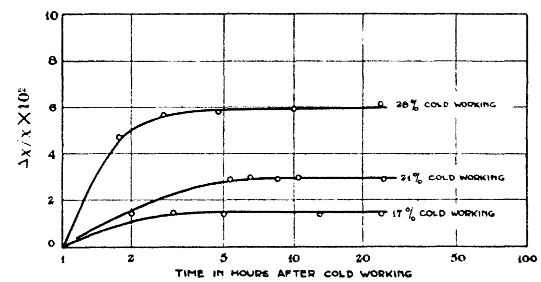

FIG. 3. Magnetic self-recovery of copper at room temperature after various degrees of cold working.

working at room temperature; if magnetic self-recovery is connected with recovery from lattice distortion, one should therefore expect to observe such recovery in copper but not in aluminum, under the present experimental conditions. It is possible that, if the aluminum were cold-worked at some *low* temperature, recovery effects might become observable in this case also.

B. Recovery in Copper as a Function of Cold Working

Some further experiments were carried out to determine to what extent magnetic self-recovery at any given temperature was affected by the degree of cold working. The results of these investigations are summarized in Fig. 3, where the percentage change in χ is shown as a function of time; as before, χ represents the susceptibility of the copper as measured one hour after cold working was carried out.

It should be remarked that, as Fig. 1 shows, the "cold-worked" value of susceptibility for copper appears to be approximately constant for all degrees of cold working between about 10 percent and 50 percent reduction of area. That is, χ in Fig. 3 has the same value (within the limits of accuracy of the measurements) for each curve given, this value being -0.072×10^{-6}. The curves all refer to a temperature of about 290°K and, since the balance and specimen remained undisturbed during any one series of measurements, the relative accuracy of the points on any particular curve is within $\frac{1}{2}$ percent.

Two significant features should be noted in these results. In the first place it is clear that the susceptibility reaches a stable value after an interval of the order of ten hours, and that the extent of the self-recovery depends on the degree of cold work, being greater for greater degrees of cold work. It amounts, however, only to six percent of χ at a 28 percent reduction of area, and from the trend of the curves it seems improbable that the self-recovery would amount to more than about one-half of the initial decrease, even if cold working were continued to 50 percent reduction. Beyond this point, as we have already noted, additional factors evidently contribute to changes in the susceptibility.

The second feature on which we wish to remark is the fact that the time required for self-recovery in these experiments does not appear to depend greatly on the extent of the cold work. In other words, the initial rate of recovery is greater for greater cold working, and at a temperature of 290°K the susceptibility appears to have reached a stable value after some five to ten hours. This time of recovery depends quite markedly, of course, on the temperature, as Fig. 2 shows.

VIII. TEMPERATURE DEPENDENCE OF SUSCEPTIBILITY OF ANNEALED AND COLD-WORKED METAL

A. Copper

In some earlier work[8] it was noted that the temperature variation of susceptibility of cold-

TABLE II. Temperature variation of susceptibility of annealed and cold-worked copper.

Cold work: percent reduction of area	Percent change in χ over temperature range 90°K to 630°K
Annealed and slowly cooled	22
Annealed and quenched	21
5.5	12
19.7	12
26.7	12.5
36.0	13

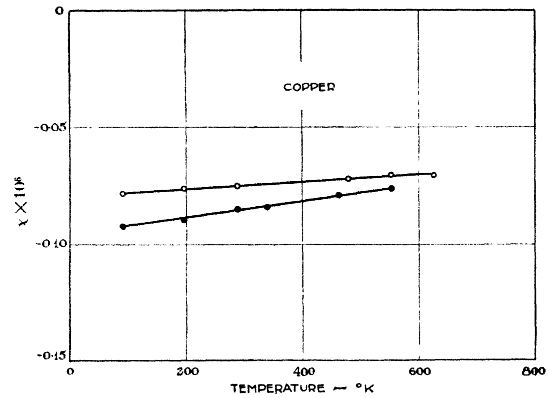

FIG. 4. Temperature dependence of susceptibility of copper. Open circles, copper cold-worked to 5.5 percent reduction of area; filled circles, copper annealed and quenched.

worked pure copper appeared to differ somewhat from that of the annealed metal, and more extensive and systematic investigations of this point are reported here. Over a temperature range from 90°K to about 630°K susceptibility was found to be, in both cases, very nearly a linear function of the temperature; but whereas the annealed metal showed a variation of χ of about 22 percent of its room temperature value over this range, the cold-worked metal showed a variation of only 12 percent. Furthermore, the amount of cold working appeared to have little effect on the form of the curve or on the magnitude of this variation, as is clear from Table II.

Figure 4 shows the susceptibility as a function of temperature in the case of the metal cold-worked to 5.5 percent reduction of area; for comparison the susceptibility of an "annealed and quenched" specimen is shown on the same diagram. It is worth remarking that no measurable difference was observed between the susceptibility *vs.* temperature curves for the "annealed and slowly cooled" and the "annealed and quenched" specimens, nor was any field dependence of χ observed in either case.

TABLE III. Temperature variation of susceptibility of annealed and cold-worked aluminum.

Cold work: percent reduction of area	Percent change in χ over temperature range 90°K to 630°K
Annealed and slowly cooled	28
14	29
33	27.5
62	28

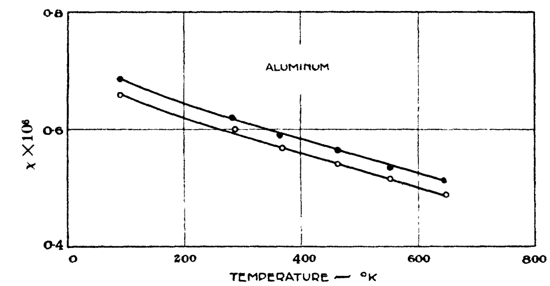

FIG. 5. Temperature dependence of susceptibility of aluminum. Open circles, aluminum cold-worked to 14 percent reduction of area. Filled circles, aluminum annealed and slowly cooled.

Throughout these measurements the specimens were always allowed to stand for 24 hours at room temperature after cold working had been carried out, so that any self-recovery would be effectively complete. The high temperature measurements were made with as little delay as possible after reaching equilibrium, so as to minimize any annealing of the cold-worked specimens. Since the recrystallization temperature of both copper and aluminum is in the neighborhood of 200°C, it is inevitable that some degree of annealing must have taken placed. However, it is believed that this must have been small over the short time during which the specimens were maintained above 200°C, because little change was ever observed in the room temperature, "cold-worked," value of χ after cooling.

B. Aluminum

Similar measurements carried out with pure aluminum showed that the susceptibility was again very nearly a linear function of temperature for both the annealed and the cold-worked metal. In this case, however, the percentage variation of χ over the temperature range used was the *same* for specimens cold-worked to various extents as for the annealed specimens. Table III shows these results. In Fig. 5 curves giving χ as a function of temperature for annealed and 14 percent cold-worked specimens are shown.

Stoner,[6] in work which will be discussed later, has developed expressions for the magnetic susceptibility of free electrons, and has shown that while any variation of electron susceptibility with temperature in a metal is very small, there would, nevertheless, be an indirect effect due to thermal expansion. This would result in an *increase* in paramagnetic susceptibility with temperature, and such an explanation appears to account reasonably well for the results observed by Sucksmith[15] for alkali metals and by Bates and Baker[16] for mercury. To apply such an explanation to our results for copper would require, however, that the thermal expansion of annealed copper should be nearly twice as great as that of the cold-worked metal. Very simple experiments show that this is not the case, and it is clear that metallurgical processes occurring during the cold working must have some bearing on the explanation of the results. Further, the paramagnetic susceptibility of aluminum *decreases* with increasing temperature.

IX. DISCUSSION AND INTERPRETATION OF RESULTS

We have already, in Section II, to some extent discussed the question as to whether or not ferrous impurities could account for the changes which are definitely observed in the magnetic susceptibility of a supposedly pure metal when it is subjected to cold work. If such impurities do exist and are present in ferromagnetic form, they should have two easily observable consequences: (a) the susceptibility should become field dependent, and (b) the susceptibility should appear more paramagnetic (in any given field) than it would be for the pure parent metal. The purity of the metals used in the present work appears to have been sufficiently high for (a) to have been eliminated, while (b) is not borne out in the case of paramagnetic aluminum.

Further, the solubility curve of iron in copper is such that the amount of iron which could be held in equilibrium in solid solution falls very rapidly as the temperature is reduced, from about 3 percent at 1000°C to an altogether negligible amount in the region of room temperature.[17] Hence, much of the iron present as impurity should precipitate out into either paramagnetic or ferromagnetic form if the metal is very slowly cooled from a high temperature. On the contrary, iron impurity can be retained in solid solution (and hence presumably in a non-magnetic form) if the metal is suddenly quenched from a high temperature. If, therefore, the supposedly pure metal contains iron impurity, it should easily be possible to observe a difference in the magnetic behavior of a specimen when slowly cooled and when quenched. No measurable differences have been observed in the present work, either in copper or aluminum.

In our discussion of the results we shall first consider what happens when an annealed metal is subjected to cold working. In general, three processes occur: (a) lattice distortion, (b) grain fragmentation, and (c) grain orientation. These effects can all be followed by x-ray investigations, as was done by Wood,[14] and the results, very briefly summarized, are as follows. For annealed, pure copper separate sharp reflection spots are obtained, grouped around the positions to be expected for Debye-Scherrer rings. On cold working, a transition to radially diffuse rings gradually occurs, and at the same time change in the diameter of the rings indicates an alteration of the lattice spacing. Wood found that the diffuseness of the rings did not exceed a certain maximum, whatever the degree of cold work, and that the lattice spacing change fluctuated in a periodic fashion.

Fluctuations in lattice spacing similar to the above were found for various other metals, but *not* for aluminum. In the case of aluminum, even after extensive cold working, the lines remained relatively sharp and perfectly resolved. This indicated that not only is the minimum crystallite size resulting from fragmentation considerably larger than in the case of copper, but also that aluminum is spontaneously self-recovering from lattice distortion during cold working at room temperature.

As already noted, recent experiments have been reported[7] showing that cold-worked pure copper also exhibits a "self-recovery" in the sense that a reduction in diffuseness of the lines in x-ray diffraction patterns occurs over a period of some hours, or even days, when the metal is maintained at room temperature. In some instances the reappearance of distinct reflection spots has been noted, indicating that some degree of recrystallization must also have occurred at room temperature.

[15] W. Sucksmith, Phil. Mag. **2**, 21 (1926).
[16] L. F. Bates and C. J. W. Baker, Proc. Phys. Soc. London **50**, 409 (1938).
[17] M. Hansen, *Der Aufbau der Zweistofflegierungen* (Verlag Julius Springer, Berlin, 1936).

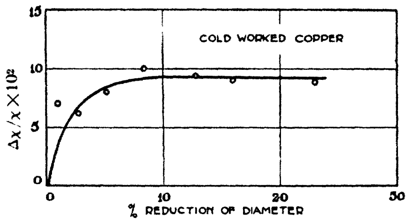

FIG. 6. Percentage change in susceptibility of cold-worked copper as surface layers of metal are removed by etching.

Reverting now to the magnetic measurements, we regard the change in magnetic susceptibility, irrespective of its direction, as due to the combined effects of lattice distortion and fragmentation; and we regard the magnetic self-recovery exhibited by copper to be a direct result of the *lattice* recovery occurring over an interval of the order of some hours. Since aluminum is spontaneously self-recovering *during* cold working at room temperature, we should not expect to find any magnetic self-recovery, but only a stable change of susceptibility due to fragmentation. These features are as we actually observe in cold-worked copper and aluminum.

On the basis of this interpretation we can say, referring again to Fig. 3, that the contribution to $\Delta\chi$ from lattice distortion in the copper increases as the degree of cold work increases, but probably does not exceed one-half of the total change in χ, whatever the degree of cold work. The remaining part of the change in χ must be attributed to fragmentation. Now, when a rod is drawn through a die, cold working is most severe in the surface layers, and it is to be expected that fragmentation is also most severe in this region. Hence, if these surface layers are removed from a cold-worked specimen which has been allowed to recover from the effect of lattice distortion, we might also expect the susceptibility to return to a value approaching that of the annealed metal.

A simple experiment to test this possibility was carried out by gradually etching away the surface from a cold-worked rod of copper with dilute nitric acid. The specimen was cold-worked to 38 percent reduction of area, allowed to recover at room temperature for about 50 hours, and then its susceptibility determined. Successively increasing thicknesses of metal were then etched from the surface, the susceptibility being measured after each etching. The results obtained are shown in Fig. 6. It will be seen that the susceptibility quickly increased (numerically) as the surface layers were etched away and had reached a constant value by the time a ten percent reduction of the diameter had been achieved. Reliable measurements could not be carried beyond about 30 percent reduction of diameter (43 percent reduction of area) because pitting of the surface then became sufficient to produce significant variations in the cross-sectional area of the rod.

It is interesting to consider the relative changes in susceptibility observed in this case. Before etching was commenced the "recovered" value of χ for the 38 percent cold-worked rod was about -0.076×10^{-6}; etching increased this value by about 9 percent, i.e., to -0.083×10^{-6}, which is approaching the observed susceptibility of the annealed metal.

Thus we have a good numerical confirmation of the suggestions outlined above to account for the change in susceptibility of copper. In the case of aluminum the observed, stable, decrease in paramagnetic susceptibility must, on this view, result from fragmentation occurring in the surface layers of the material. It is of interest to note the actual thickness of surface layer removed in the copper specimen before the susceptibility regained its value of -0.083×10^{-6}. The initial diameter of the rod after 38 percent cold working was about 3 mm. A ten percent reduction of this diameter results in removal of a surface layer 0.15 mm thick. Now several investigations[18] by x-ray methods have been carried out to determine how far below the surface of a machined piece of metal the effect of the cutting tool extends. In copper and aluminum subjected to typical machining processes it has been found that the cold work is evident to a depth of approximately 0.25 mm below the surface. This is sufficiently close to the value observed for the "depth of penetration" of the magnetic effect to suggest that the stable portion of the susceptibility change is confined mainly to the region suffering greatest fragmentation.

We are now in a position to remark further on

[18] See, for example, A. Taylor, *Introduction to X-ray Metallography* (Chapman and Hall, Ltd., London, 1945), p. 244.

the form of the curve for copper in Fig. 1, where cold working in excess of 50 percent has been carried out. Normally, recrystallization of a cold-worked metal does not occur until its temperature has been raised above some fairly well defined value which we know as the recrystallization temperature. However, it is well known that if the cold working becomes sufficiently severe, then recrystallization may commence, *even at room temperature.* It is suggested that such "spontaneous recrystallization" at room temperature begins to occur in our specimens of copper when the cold working exceeds about 50 percent reduction of area. Such recrystallization would, if our picture of the process is correct, result in a progressive increase (numerical) in susceptibility as the cold working increased beyond 50 percent. This ultimate increase in susceptibility has been observed in a number of specimens cold-worked beyond 40 to 50 percent reduction of area, and the explanation appears to lie in the direction indicated above. It is very difficult to see how ferromagnetic impurities could revert to non-ferrous form merely as a result of recrystallization at room temperature.

In this discussion we have not so far mentioned the grain orientation which occurs when a rod of polycrystalline metal is cold-drawn. It is well known from x-ray investigations that in cold-drawn wires the crystal grains become so arranged that a definite crystallographic direction tends to lie along the axis of the wire. If the crystal were magnetically anisotropic, this orientation would naturally result in a variation of magnetic properties as the metal was cold-worked. Although in their normal state crystals of both aluminum and copper are isotropic, we do not know to what extent the lattice distortion occurring during cold working may affect this isotropy. It is perhaps possible that that part of the change in susceptibility which we have attributed to lattice distortion may ultimately be related to an actual magnetic anisotropy, but at the present stage of investigations this cannot be regarded as more than speculative.

We have confined our attention so far to a consideration of those processes occurring during cold working which probably give rise to changes of magnetic susceptibility. We shall now consider the manner in which these processes could affect magnetic properties.

The magnitude of the changes in susceptibility brought about by cold working is of the same order as the value of susceptibility calculated by Stoner[6] for free electrons. The electrons in a metal cannot be regarded strictly as "free" electrons, but for many purposes may be considered as approximating to that state, and it is natural to seek first for an explanation of the strain sensitivity of susceptibility along the lines of a variation in the contribution made to the susceptibility by the electrons in the metal. Stoner has derived the following expression for the gram atomic susceptibility of free electrons.

$$(\chi_A)_e \times 10^6 = 32.1(q/V_0) \times \{1-6.11\times 10^{-9}(T/V_0)^2\}, \quad (3)$$

where q is the number of free electrons per atom and V_0 is the maximum electron kinetic energy (in electron volts) at absolute zero. For free electrons V_0 is given by

$$V_0 = 3.62\times 10^{-15}(q\cdot n)^{\frac{2}{3}}, \quad (4)$$

where n is the number of atoms per unit volume. Equation (3) implies that $(\chi_A)_e$ should decrease with increasing temperature; actually the decrease would, under ordinary conditions, be altogether inappreciable, but Stoner has shown that thermal expansion may change the value of V_0 in such a way as to produce a significant *increase* in $(\chi_A)_e$ with temperature. Thus, for an annealed pure metal we have, from (4),

$$V_0 \propto n^{\frac{2}{3}},$$

and hence, from (3),

$$(\chi_A)_e \propto 1/V_0 \propto n^{-\frac{2}{3}} \propto (1+\tfrac{2}{3}\alpha_v\cdot T),$$

where α_v is the coefficient of cubical expansion and T the temperature. Hence we have, approximately,

$$\Delta(\chi_A)_e/(\chi_A)_e\cdot\Delta T = \tfrac{2}{3}\alpha_v. \quad (5)$$

This formula accounts fairly well for the observed variation of χ with temperature for the alkali metals[15] and for mercury.[16] Clearly, the temperature variation of χ for aluminum cannot be explained in this way, nor can the difference between the temperature variations of χ for annealed and cold-worked copper. In the former case the variation is in the wrong direction, and in the latter it would require a coefficient of expansion for the annealed copper 100 percent greater than for the cold-worked metal. Experiments show that the maximum difference in the coefficient of cubical expansion is in the region of 5 percent. This failure to account for the experimental results is not unexpected however, considering the appreciable departure from "free" electron conditions which may exist in these metals.

Referring again to Eqs. (3) and (4) we see that, if we neglect the temperature dependent term in (3), we can write

$$(\chi_A)_e \propto q/V_0 \propto (q/n^2)^{\frac{1}{3}}. \quad (6)$$

Hence $(\chi_A)_e$ will vary with cold working of a metal if either q or n varies. Now we can easily see that both q and n *do* vary when the metal is cold-worked; and whether or not $(\chi_A)_e$ increases or decreases due to the cold working will depend on the relative changes in q and n^2.

When a metal is subjected to cold working, grain fragmentation occurs, with consequent increase in grain boundaries and regions of considerable internal strain. It is generally agreed that grain boundaries and centers of strain form regions in which the "free" electrons of the metal may become "trapped" or perhaps partially bound. Such a trapping of electrons would result in a decrease in the effective value of q and hence of $(\chi_A)_e$. On the other hand, cold working results in a decrease in the density of a metal;[5,19] this implies a decrease in n, which in turn results in an increase in $(\chi_A)_e$. It easily follows from (6) that the fractional *decrease* in electron paramagnetism on cold working would be given by the expression

$$1-\{(q/q_0)\cdot(\rho_0/\rho)^2)\}^{\frac{1}{3}}, \quad (7)$$

where ρ is the density and the subscript "0" refers to the annealed metal. Whether the cold-worked metal appears more or less paramagnetic than when in the annealed state will obviously depend on whether the cube root term in (7) is greater or less than unity. Clearly, therefore, the change in susceptibility could be in either direction, depending on the extent of electron trapping relative to the change in density. Trapping of electrons implies, of course, that q is less than q_0; however, in a cold-worked metal ρ_0/ρ is always slightly greater than unity, so that the sign of the term (7) as a whole will depend on the metal itself.

If we accept the density measurements of Shimizu[5] it appears that $(\rho_0/\rho)^2$ for copper is appreciably greater than for aluminum for similar degrees of cold working. Furthermore, aluminum has three electrons outside a neon-like core while copper has only one outside a newly completed 3*d* shell. Therefore it might not be unreasonable to suppose that trapping of electrons could occur more easily in aluminum than copper; in other words, q/q_0 could conceivably be relatively less for aluminum than for copper. Both effects would tend to make the cube root term of (7) relatively greater for copper than for aluminum, with the possibility that the whole term (7) may be positive for aluminum but negative for copper. Such would be in accordance with our observations. However, it is unjustifiable to carry speculation beyond this stage at present; not only have we neglected to consider what the effect of the "trapped" electrons may be, but also we know little as yet of the actual mechanism by which trapping may occur in cold-worked metals. Nevertheless, the degree of correlation which can be achieved along the lines indicated leads us to consider that the explanation of strain sensitivity of magnetic susceptibility may lie in this direction.

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[19] S. L. Smith and W. A. Wood, Proc. Roy. Soc. **A179**, 450 (1942).