THE MAGNETIC ISOTROPY OF COPPER CRYSTALS*

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Abstract

The variation in the magnetic susceptibility with the direction of the applied field was investigated for large single crystals of copper. A modification of Curie's method of measurement was used. A Fourier analysis of the results indicates that there is no variation of susceptibility larger than 1%, a result consistent with the magnetic isotropy of cubic crystals predicted by the theory of W. Thomson.

I. Introduction

SINCE its conception in 1851, the description by means of the familiar ellipsoid of magnetization of the variation of the magnetic susceptibility of a non-ferromagnetic crystal with respect to the direction of the applied magnetic field has been accepted as correct until quite recently. It follows from this theory that for substances which form cubic crystals, there can be no dependence of the magnetic susceptibility upon direction of applied field so that the material must be magnetically isotropic.

In 1926, J. Forrest[1] performed some qualitative experiments on a number of cubic crystals and found that they were not isotropic, but that they showed variations in susceptibility as do single crystals of iron and nickel. McLennan and Cohen[2] investigated the magnetic susceptibility of large single crystals of a number of metals, and found that while bismuth seems to follow a law of variation with the direction of the magnetic field in accord with the accepted theory, antimony deviates noticeably from it. In addition, recent work[3] on the Peltier and Thomson effects, which should obey the same symmetry relations as the magnetic susceptibility, seem also to show a deviation from the theory. Thus the accepted theory may have a more limited range of application than hitherto supposed, and it was deemed advisable to reinvestigate a cubic crystal, and to determine whether or not it is magnetically isotropic.

II. Apparatus and Method of Measurement

In order to measure the susceptibilities of crystals it was decided to use a modification of Curie's method which has been developed to quite an extent by P. Weiss and his collaborators, a description of the final apparatus

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[1] J. Forrest, Trans. Roy. Soc. Edinburgh **54**, 601–701 (1926).

[2] J. C. McLennan and E. Cohen, Trans. Roy. Soc. Canada [3] **23** III, 159–168 (1929).

[3] H. D. Fagan and T. R. D. Collins, Phys. Rev. [2] **35**, 421–427 (1930); P. W. Bridgman Proc. Amer. Acad. **63**, 351–399 (1929).

being given by Foex and Forrer.[4] The apparatus described below differs from theirs in several details.

A beam, 90 centimeters long, composed of three parallel lengths of quarter inch balsa wood, fastened at the ends and in the center at the corners of equilateral triangles, is suspended by five silk threads approximately 50 centimeters in length. These five suspensions are arranged so as to permit translation of the beam only in the direction of its length. They are hung at the top from a heavy iron frame in such a way that their lengths can be separately adjusted. The lower member of the beam is extended at one end and carries a small piece of aluminum with a vertical hole drilled in it about 2 centimeters deep. Into this hole fits the shaft of a crystal holder on which the crystal is placed. The crystal holder consists of a 7 centimeter length of #16 sterling silver wire on which fits a small cylindrical cap of amber, cut away at the top to fit the crystals, and graduated on the side every 10°. These graduations could be observed by means of a reading microscope and the azimuth of the holder thus read off. An electromagnet capable of producing fields up to about 5000 gauss was used. It was equipped with special pole pieces so as to obtain a field which has a high value of the product of the field by its derivative over a large area. Under the crystal holder, a small saddle, constructed out of copper wire and a small piece of paper, was fastened. This could hold either the crystals or the standard on the beam but was out of the field while measurements were being taken.

The other end of the balsa wood beam carried a celluloid cylinder 6 centimeters in diameter and 15 centimeters long, closed at one end, into which fits a piece of wood with a clearance all around of about 4 millimeters. This provides air damping which, combined with the electromagnetic damping of the sample in the field, is quite satisfactory.

At the center of the beam and perpendicular to it, is an aluminum arm extending some 10 centimeters out, to which is firmly waxed a phonograph needle pointing in the direction of the beam. This needle rests against and perpendicular to a microscope cover glass 1 centimeter in diameter. This is attached to the back of a galvanometer mirror suspended at both ends by a tightly stretched vertical quartz fiber of diameter about 50 microns. The plane of the cover glass makes an angle of 135° with the mirror. Light from an illuminated cross hair is reflected by the mirror and falls on a scale some two meters distant. Thus this arrangement acts as an optical lever and gives a total magnification of the motion of the beam of about 1000 times. The whole arrangement was placed in a wooden box having a large glass window on the side in order to stop air currents. The box was put on a stone pier in a sub-basement room to avoid mechanical vibrations.

When current is passed through the magnet coils, a force is exerted on the specimen and the beam will deflect until the force of gravity balances out the magnetic force. Suppose to do this the beam moves a distance x, and let l be the effective length of the suspensions, m the total mass of the suspended system, f the magnetic force, and g the acceleration of gravity.

[4] G. Foex and R. Forrer, Jour. de Physique [6] **7**, 180–187 (1926).

Then

$$x = fl/mg \qquad \text{when } x \ll l.$$

Now if the crystal has a susceptibility* k in the direction of the field, we have

$$f = \int kH_y \frac{\partial H_y}{\partial x} dv$$

where the x-axis is in the direction of the beam, the y-axis in the direction of the field, and the integral is taken over the volume of the crystal. Now if the variation of f with respect to x is small, then

$$x = Ak$$

where A is a constant. Hence, if we have a substance with a known value of the susceptibility, we can measure the susceptibility of any other substance by determining the value of A.

In order to test the validity of the assumption that f does not vary appreciably with the position of the crystal, a series of values of x were measured for various values of the field strength. We see from the above equations that

$$x \sim H_y \frac{\partial H_y}{\partial x} \sim H^2$$

if the assumption is justified, and hence if we plot values of x as a function of H^2 we should get a straight line through the origin. With values of the field strength measured in arbitrary units by a ballistic method, we find that within the limits of accuracy of a reading, we do get such a straight line.

Measurements were made of the variation of susceptibility of single crystals of copper as a function of the azimuth of the field. Gold was used as the standard substance. We see that to compare susceptibilities of two substances by this method we must keep the mass of the beam constant. Hence the following procedure was followed in measurement. The gold standard was placed in the paper saddle, and a copper crystal in the crystal holder. Then a series of deflections of the spot of light was observed for 36 azimuths of the crystal. Then the crystal was removed and placed in the saddle, while the gold was placed in the holder. A series of deflections for four azimuths was then taken. Then both the crystal and the gold were placed in the saddle and the deflections due to the holder alone were observed for the same four azimuths.

The zero shift over the whole period of time required for one such set (about ten hours) was not more than 50 to 75 millimeters.

III. Preparation of Specimens and Determination of their Orientation

The copper crystals used in these experiments were obtained from the Hammond Metallurgical Laboratory, Yale University, through the courtesy

* This is not a true susceptibility, but the difference between the susceptibility of the crystal and the surrounding medium, in this case, air.

of Dr. C. H. Mathewson. They were prepared[5] from the highest purity electrolytic copper by slowly lowering a graphite crucible containing the molten copper out of an induction furnace whose temperature at the center was maintained well above the melting point of copper. The rate of lowering was about 0.6 centimeter per hour. The single crystals so obtained were in the form of rough cylinders approximately a centimeter in diameter and 12 to 15 centimeters long. When these rods were etched in a 50 percent solution of nitric acid for a short time, and then washed, the surface of the rod would shine out brilliantly when held at certain positions with respect to parallel incident light. This is due to the fact that the etching process forms micro-

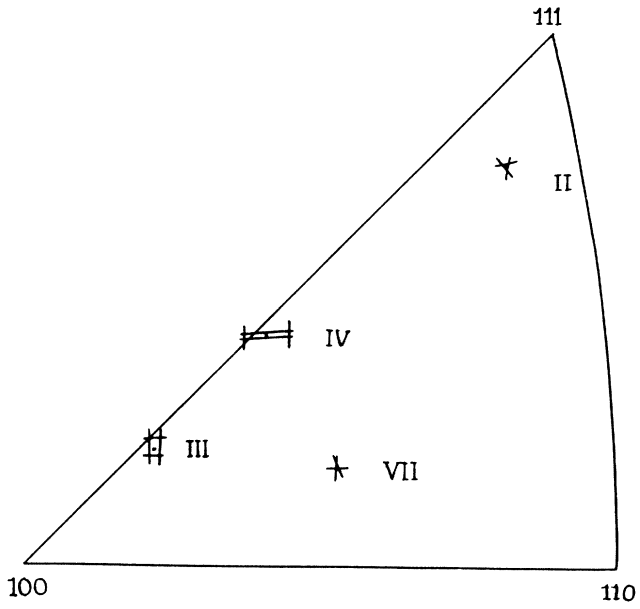

Fig. 1. Stereographic projection of the axes of the crystal rod.

scopic pits in the surface whose sides are definite crystal planes, and it is the light reflected from these pit-faces that gives rise to the selective reflection. It is evident that if the positions of these faces with respect to the rod as a whole could be determined, and the crystallographic form of these faces identified' then the orientation of the crystal lattice with respect to the rod as a whole could be obtained. Bridgman[6] has described one method of accomplishing this, but a more convenient, if not more accurate, arrangement was used here. The lenses were all removed from the telescope tube of a large polarizing spectrometer, and a plane piece of glass was fastened to the end of the telescope so that the normal to its plane was horizontal and made an angle of 45° with the axis of the telescope. The crystal rod was mounted horizontally and attached to a vertical circle carried by the

[5] C. H. Mathewson and K. Van Horn, A. I. M. E. Tech. Pub. No. 301-E-109, Feb., 1930.
[6] P. W. Bridgman, Proc. Amer. Acad. **60**, 305–383 (1925).

collimator tube. The light of a small carbon arc with condensing lenses was thrown on the piece of glass on the telescope and reflected to the crystal. By changing the position of the crystal with respect to the light beam, it could be adjusted so that the light from a reflecting surface could be viewed through the telescope. The spherical coordinates of the normal to the pit-face could then be read off the horizontal and vertical circles. The points corresponding to these coordinates were then drawn on a 15 centimeter marble sphere, and the crystallographic planes corresponding to each reflection maximum could be identified. The position of the rod axis with respect to the crystal lattice was then determined by plotting the observed angles on a stereographic net.

Considerable difficulty was sometimes experienced in getting reflections which could be unambiguously identified. The etching process seems to be a difficult one to control satisfactorily, a condition due to the fact that the reaction is a complicated one and particularly dependent upon the amounts of the end-products present in the etching solution. Various concentrations of nitric acid were tried, and consistent results were obtained more often with a 50 percent by volume solution than with any other. Figure 1 shows the stereographic projection of the rod axes of the crystals used.

The specimens were prepared by cutting off a section from the long rod. In order to cut the single crystal rods without spoiling them by introducing too large strains, the following method was used. Two vises were set up and the jaws accurately aligned on the bench of a milling machine. The rod was well padded with paper and held firmly in one vise between two V-blocks. In the other vise was held a jig consisting of two guide slots attached to a piece of steel at right angles to its length. A hack saw blade, 0.025 inch (0.064 centimeter) thick, with all the set removed from the teeth, fitted into these two slots and could be moved only in the plane defined by them. From 30 to 40 minutes were taken to make a cut, and plenty of oil was used. When a section had been cut off, the burr was removed with a fine file and the surface removed in a 50 percent nitric acid solution until the characteristic shine was restored. Care had to be taken to keep the crystals away from moist air, as they tarnished quite rapidly.

The following table gives the dimensions of the crystals used.

Crystal	Diameter	Length	Mass
II	0.764 cm	0.991 cm	3.921 gram
III	0.767	0.968	3.849
IV	0.770	0.993	4.057
VII	0.772	0.942	3.927
Gold Standard	0.770	0.975	8.752

As a substance of standard susceptibility, a piece of gold was used. It was obtained from Baker and Co. who stated that the purity was over 99.99 percent. A piece was machined out whose size was close to that of the crystal specimens. The value of the susceptibility chosen was that obtained

by Owen,[7] viz., -0.141×10^{-6} cgsm. This same value was obtained by Seeman and Vogt,[8] who have recently investigated copper-gold alloys.

No traces of ferromagnetic impurity could be detected in either the copper crystals or the gold standard.

IV. Reduction of Observations and Results

In order to insure that the copper crystals used were sufficiently representative, average values of the susceptibility were obtained for each. Taking into account small corrections due to the magnetic effect of the crystal holder and of the air, we get the following values of the specific susceptibility of the different crystals:—

Crystal	$\chi_{Cu}\cdot10^{6}$
II	−0.088
III	−0.075
IV	−0.086
VII	−0.091
Mean	−0.085

The spread of values here is just about that to be expected. Owen[7] gives the value

$$\chi_{Cu} = -0.085\cdot10^{-6}.$$

In order to bring out any possible anisotropy in the susceptibility of copper it is sufficient to use relative values of the susceptibility only. The values of the deflections obtained with a crystal in the holder were therefore subjected to a Fourier analysis, obtaining the coefficients of the first four cosine and the first four sine terms.

We obtain the following results in millimeters.

$$\begin{aligned}
x_{\text{cu II}} &= 76.31-1.88\cos\varphi-0.68\cos2\varphi-0.36\cos3\varphi\\
&\quad+0.30\cos4\varphi-0.68\sin\varphi-0.44\sin2\varphi\\
&\quad+0.11\sin3\varphi-0.61\sin4\varphi,\\
x_{\text{cu III}} &= 68.85-2.41\cos\varphi-0.36\cos2\varphi+0.08\cos3\varphi\\
&\quad-0.05\cos4\varphi-0.39\sin\varphi-0.16\sin2\varphi\\
&\quad-0.07\sin3\varphi-0.05\sin4\varphi,\\
x_{\text{cu IV}} &= 75.88-0.95\cos\varphi-0.29\cos2\varphi+0.16\cos3\varphi\\
&\quad-0.03\cos4\varphi-0.45\sin\varphi+0.36\sin2\varphi\\
&\quad+0.15\sin3\varphi+0.03\sin4\varphi,\\
x_{\text{cu VII}} &= 76.30-0.87\cos\varphi-0.26\cos2\varphi+0.38\cos3\varphi\\
&\quad+0.02\cos4\varphi+0.24\sin\varphi+0.41\sin2\varphi\\
&\quad+0.01\sin3\varphi+0.00\sin4\varphi,\\
x_{\text{cu III}}' &= 68.92+1.02\cos\varphi-0.16\cos2\varphi-0.08\cos3\varphi\\
&\quad+0.00\cos4\varphi-1.96\sin\varphi+0.01\sin2\varphi\\
&\quad+0.02\sin3\varphi+0.03\sin4\varphi,
\end{aligned}$$

where φ is the azimuth as read. $x_{Cu\ III}'$ is a set of measurements made on crystal III in a different holder.

[7] M. Owen, Ann. der Physik [4], **37**, 657–699 (1912).

[8] H. J. Seeman and E. Vogt, Ann. der Physik [5], **2**, 976–990 (1929).

Figure 2 gives the observations for crystal III plotted as a function of the azimuth φ. The curve drawn is $A_0+A_1 \cos \varphi+B_1 \sin \varphi$ as determined by the least squares analysis. Due to the fact that it was impossible to secure a holder which was perfectly straight and vertical, the crystal did not rotate exactly about its axis of figure. This gives rise to the large 360° period which the results show. That this is the case is supported by the fact that the 360° periods obtained by the least squares analysis are in close agreement in phase, with the exception of $x_{\text{cu III}}'$ which was made, as has been stated, with a different holder. An additional cause which contributes to this 360° period and may explain a shift in phase is the fact that the crystals were not exactly right circular cylinders. Thus we ascribe the whole of the 360° period to instrumental error. It is impossible to assign a crystallographic basis to the 360° period without attributing hemihedry to copper, for which there is, of course, no shadow of evidence.

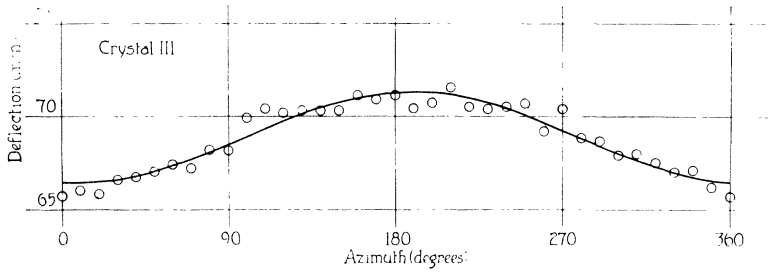

Fig. 2. Values of the deflection of the beam plotted against the azimuth of the crystal.

If there is any anisotropy, it must have four-fold symmetry about a $<100>$ axis, three-fold symmetry about a $<111>$ axis, and two-fold symmetry about a $<110>$ axis. These are all the symmetry properties of a cubic crystal. Now, if without touching the apparatus we repeat a reading, on the average we will find that it cannot be reproduced closer than 0.5 millimeter. This is indicated on Fig. 2 where the diameter of the circles representing the observations gives what we may call the limits of "immediate reproducibility" of an observation. This represents a sort of minimum probable error. The actual probable error is much larger, as other factors such as the variation of temperature and humidity, which affect the length of the fibers, must be considered in assigning a proper value to the probable error. If we take this value of 0.5 millimeter as the minimum probable error, then we can compute from it the probable error in a coefficient of the Fourier series. For a series, representing 36 observations the probable error of a coefficient of a harmonic term is 0.236 times the probable error of a single observation, i.e., in the present case, 0.12 millimeter.

Now the axis of figure of crystal III lies near a $<100>$ axis. Hence, if any anisotropy exists, we should expect a large term in 4φ. We see that the coefficient is actually less than half of the minimum probable error of that coefficient, i.e., it is sensibly zero. By the same reasoning the terms in 3φ are also sensibly zero. There is no physical justification for such terms.

In crystal II, whose axis of figure is close to a $<111>$ axis, we should expect a large term in 3φ. Actually, the 4φ coefficient which has no significance for a three-fold axis, is larger than the 3φ coefficient, and the fact that both coefficients are larger than our minimum probable error should not therefore be taken as significant. We can therefore say that no three-fold symmetry can be detected with any degree of certainty. In a similar way the 3φ and 4φ coefficients of the more unsymmetrical cases of crystals IV and VII may be regarded as negligible.

It is to be noticed that in all cases the terms in 2φ have amplitudes larger than our assigned error. These can all safely be considered as due to the "spread" of the points. That is, we have chosen too small a value to represent our probable error. If we choose an error twice as great, viz., 1.0 millimeter, the probable errors in the 2φ terms become as large as the terms themselves.

We can therefore only ascribe any physical reality to the terms of period 360°, and these, it seems, are wholly due to instrumental defects. To assign a *limit of error* to this work it is only necessary to notice that the coefficients of terms of shorter periods than one revolution are all less than 1 percent of the whole effect, viz., less than about 0.7 millimeter. This represents, of course, not the probable error in a coefficient, but rather a limit of error; the actual probable error is less than this.

It is to be concluded from the experimental work described above that single crystals of copper show no variation of their diamagnetic susceptibility with the direction of the applied magnetic field greater than 1 percent.

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