susceptibility. The value computed for this quantity using Hylleraas' function, ψ_C,[6] is 2.46, a value which may be accepted as nearly correct. Since in computing this quantity it is desired to minimize long range errors the most reliable results should be obtained, according to our argument, by minimizing ϵ/δ^2, the least reliable by minimizing δ^2. Actually the deviations from the correct answer have the corresponding order.

[6] The radial charge distribution corresponding to this function is given by Bethe, Zeits. f. Physik **55**, 431 (1929).

It is interesting to compare these results with those for ψ_B. The low value of $\kappa^2\epsilon_x$ given by ψ_B indicates that the low value of ϵ compared to the values given in Table II, is due to reduction of short range errors. (ψ_B takes some account of the relative positions of the electrons, whereas ψ_A and the above functions do not.) Despite the smaller energy error, therefore, this is not a favorable function for the computation of $(r_1^2)_{Av}+(r_2^2)_{Av}$; actually, it gives the value 1.76, lower than any other computed.

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Magnetic Analysis of Evaporated Bi Deposits

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The magnetic susceptibility of evaporated bismuth films ranging in thickness from 0.1μ to 4μ has been measured by a compensated Gouy method in conjunction with a Sartorius microbalance. Films above 0.5μ are found to have a susceptibility, independent of film thickness, whose value agrees well with that of a single crystal with trigonal axis parallel to the field. Below 0.5μ the susceptibility decreases as the film thickness is reduced. It is suggested that films below 0.5μ possess a microcrystalline fiber structure which merges into a phase of macrocrystalline structure above this thickness. If films less than 0.5μ were aged for long periods in vacuum an increase in the susceptibility was noted, whereas no such effect was observed when thicker films were similarly treated, the effect being ascribed to a recrystallization process. The susceptibility of thick films ($>0.5\mu$) was found to be identical when deposited, respectively, on glass, Au, Cu and Sn. The nature of the crystalline aggregate, as determined from the susceptibility, was found to be dependent on the amount of residual gas present in the apparatus when the films were deposited. As the gas pressure, during deposition, was increased from about 10^{-5} mm of Hg the susceptibility measured with the field parallel to the film normal was greater than the same quantity measured in films produced in high vacuum. The susceptibility measured when the field was perpendicular to the film normal, on the other hand, remained approximately the same in the two cases. At relatively large gas pressures (*ca.*10^{-2} mm) the resulting films possessed a susceptibility which was independent of the angle between the film normal and the magnetic field. The bearing of these results on the structure of the deposits is briefly discussed.

INTRODUCTION

THE question as to whether metallic condensates possess crystalline structure or are amorphous aggregates of atoms has, for some years, been a matter of considerable controversy. Such layers as are produced, for instance, by evaporating metal onto a cold surface in vacuum possess a number of abnormal properties as compared with bulk metal. Among these may be mentioned their very high specific resistance, and the fact that it has often been difficult or impossible to obtain from them sharply defined x-ray patterns.

In recent years such layers have been the object of renewed investigation by electron diffraction.[1] A number of such investigations have shown that evaporated films possess a crystalline structure, even down to thicknesses of a few atomic layers, the lattice spacing being identical with that of the bulk material. Kirschner found that such layers often possessed preferred orientation and that the films appeared to be composed of individual crystallites with linear dimensions, for very thin films, of the order of 10A, the particle size increasing as the thickness of the layer increased. Heating the films tended to sharpen up the diffraction lines, that is to say, the crystal

[1] F. Kirschner, Zeits. f. Physik **76**, 576 (1932).

grains increased in size or became more perfectly arranged, or both.

Recently the production of films with electron diffraction pattern like that of a single crystal, has been reported.[2, 3] These layers, up to the limiting thickness produced, 0.1μ, consist of large numbers of crystals (average size from 0.001μ to 0.01μ) all orientated alike. The resulting films are therefore really mosaic monocrystals. Furthermore the investigators have shown that the temperature of the surface upon which the vapor is condensed determines whether one gets such a single crystal or not. In general there is a pseudo-critical temperature, characteristic of the metal, below which it is not possible for form a "single crystal" film.

In the particular case of bismuth no observations have been reported by Lassen and Bruck but new observations on the crystalline nature of this metal have been published recently by Goetz, Stierstadt and Focke.[4] These authors have investigated thick Bi layers (>0.1 mm) by an optical method. If a section of the deposit taken perpendicular to the backing surface be examined under a high power microscope two distinct layers are seen. The first, starting at the backing surface and extending out for about 100μ, has grains, if any, so small as to appear "amorphous" and the second layer rooted in this one appears as a conglomerate of fine parallel needles, each obviously a single crystal. The transition between the two layers is very abrupt. The "amorphous" layer remains virtually unresolved even up to the highest magnification employed (some 1500 diameters). On the basis of these observations the authors conclude that the "amorphous" layer consists of crystalline Bi of extremely small particle size (microcrystalline layer). The second layer on the other hand consists of large orientated crystals (macrocrystalline layer). From what has been said previously about electron diffraction experiments it is apparent that this explanation is qualitatively plausible. The fact that this microcrystalline layer extends to thicknesses of as much as 100μ is, however, very surprising, since as has been mentioned the particle size increases as the film thickness is increased, even far below this thickness. Very small particles are associated with very thin films and on this scale of measurement films greater than about 1μ must be regarded as "thick."

It seemed desirable, therefore, to examine this problem by a third method, entirely different from those mentioned above. It appeared that absolute measurements of the magnetic susceptibility of Bi films would provide considerable information about these matters. For one thing, the susceptibility of Bi varies with crystal orientation and the nature of this variation is well known, so that preferred orientation of microcrystals might be quantitatively estimated. Again there is good evidence in support of the fact that microcrystalline Bi has a smaller susceptibility than macrocrystalline.[5] Bismuth particles less than about 1μ have a susceptibility less than the bulk material, as the particle size is decreased below this limit the susceptibility decreases roughly proportionally. This makes it possible to follow changes in mean particle size at very small sizes. And finally amorphous Bi should have a susceptibility some 20 times less than the regulus material, so that if any considerable fraction of the film were amorphous the fact could not escape notice. In general an interpretation of the crystalline nature (or otherwise) based on susceptibility measurements should be unambiguous.

Technique

The bismuth used in this work was supplied by Eimer and Amend and had a stated purity of 99.98 percent without, however, an analysis showing the amounts of individual impurities. This stock metal was, however, subjected to magnetic tests, discussed later, which showed it to be highly pure from a magnetic point of view. The films were produced in high vacuum by evaporation from a small furnace, through a series of collimating slits. The actual design of this equipment will not be further discussed here since similar apparatus containing all the essential features has already been described.[6] Particular pains were taken to insure that all films

[2] H. Lassen and L. Brück, Ann. d. Physik **22**, 65 (1935).
[3] L. Brück, Ann. d. Physik **26**, 233 (1936).
[4] A. Goetz, O. Stierstadt and A. B. Focke, Zeits. f. Physik **98**, 118 (1936).
[5] S. Rao, Ind. J. Phys. **6**, 251 (1931); **7**, 38 (1932).
[6] C. T. Lane, Phys. Rev. **48**, 193 (1935).

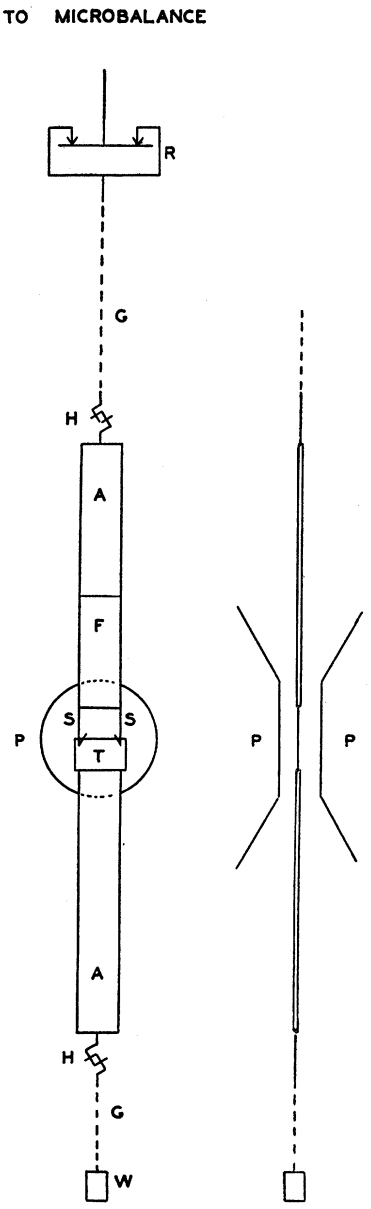

FIG. 1. Schematic diagram showing the method of measuring the susceptibility of thin films.

were produced under as nearly identical conditions as possible. Furnace temperature and residual hydrogen pressure in the apparatus were rigorously controlled and the films were "aged" by filling the apparatus with hydrogen at atmospheric pressure as soon as the evaporating process was complete. It has been mentioned previously that an absolute measurement of the susceptibility was desirable and of the several methods available for such measurement the Gouy method is by far the simplest and most reliable. This method consists in measuring the logitudinal force on a long prism of the substance, one end of which is in a strong magnetic field, the other end being in a field of much lower intensity. In the case of a thin film two special difficulties present themselves. The first, and least important of these, is that, since the amount of matter of which the film is composed is very small, the resultant force on it in the strongest available magnetic fields will likewise be very small. This trouble was overcome by using a Sartorius microbalance which would measure 2×10^{-6} g as a lower limit. This balance also conveniently measured the total weight of the film. The second difficulty lies in the fact that any substance upon which it is practical to deposit the film will itself experience in a magnetic field a force some hundreds of times larger than that upon the film itself. In order, then, to measure the film susceptibility with any degree of accuracy it is apparent that its backing must be magnetically compensated to a high degree. That is to say, the effective susceptibility of the backing must be reduced to as low a figure as possible. Fig. 1 indicates in a schematic manner the way in which this was brought about. *AA* are two glass microscope cover slips approximately 10 cm long, 2 cm wide and 0.01 cm thick. One of these slips has three glass hooks *S*, *S*, *H*, fused directly on to it. The other has a glass trapeze *T* at one end and a hook *H* at the other. This "glass blowing" was done with a gas flame a few mm long. This system is suspended from a small rotation head *R* which in turn is suspended from one arm of the microbalance. By means of *R* the film normal can be set at any desired angle to the magnetic field. A small gold weight *W* is used to keep the glasses straight. *G* is a very fine gold chain. The positions of the magnet pole pieces are indicated in the sketch (*P*). Evidently this system will have an effective susceptibility of zero provided the two glasses *AA* are alike in dimensions and in susceptibility in the parts extending beyond the uniform field at the center, supposed to extend over the hooks and trapeze, and provided further that the field intensities at the upper end of *A* and at the lower end of *A** are zero. In actual practice, small differences in the two glasses, asymmetry in the

magnetic field, etc., resulted in the system having a small effective susceptibility. This was corrected by depositing a film of gold on one or other of the glasses depending on whether the net susceptibility was positive or negative, the appropriate thickness of this gold deposit being determined empirically. The Bi film (F) was then deposited on the other glass. It is evident that small traces of ferromagnetic impurity at any part of the system would completely upset its compensation and hence very considerable care had to be exercised in the choice of materials. Only very pure diamagnetic materials were used and each piece was inspected magnetically before being selected for use.

The hooks made it possible to remove the system and replace it in virtually its original position in the magnetic field. The system used in the final measurements was acted upon by a residual force, in a field of maximum intensity about 28,000 gauss of the order of 5×10^{-6} g (equivalent susceptibility, 10^{-9}) and it was found possible to repeat its compensation to within this limit when the glass strips were removed and replaced. In carrying out an actual measurement the following procedure was followed. The system was set up, compensated, removed, and a Bi film deposited upon one of the glasses. After measuring the force on the film in the maximum field allowed by the set-up the system was again removed, the bismuth film was dissolved away in dilute HNO_3, the system replaced, and the compensation rechecked. If any significant change was found to have occurred this set of data was thrown out. In about 5 percent of the actual trials it was found that the compensation had changed. The most frequent source of such changes was probably incomplete demagnetization of the magnet, which varies the change in pull upon remagnetizing to the measured maximum intensity.

The majority of the measurements was made with the plane of the film perpendicular to the field since in this case the magnet air-gap was least, giving highest field and greatest sensitivity. When it was necessary to investigate the variation of susceptibility with angle between film normal and field a wider gap had to be employed. In this case significant measurements could only be made on relatively thick films. In using a balance of high sensitivity the control of the temperature is naturally of great importance. In the present case triple shielding was resorted to. The system was suspended with its center 50 cm below the balance arm in a narrow rectangular trough made of three vertical strips of brass. Surrounding this and also enclosing the pole pieces was a base made of plywood. Surrounding the whole water-cooled magnet was a third casing of beaver board. A heavy slate shelf, which supported the microbalance, served as the roof of this last mentioned housing. The microbalance itself was shielded by heavy cardboard. Finally, when measurements were being made, the temperature of the whole room (a small one) was kept as constant as possible.

In order to arrive at an absolute value for the susceptibility it is of course necessary to know the field strength at each end of the film. To measure this ballistically in a region where the field gradient is large (as it is at the end of the film not in the magnet air-gap) presents considerable difficulties. It appeared better to measure the desired function of the magnetic field intensities by the force on a substance of known susceptibility. To this end some extruded polycrystalline wires, about 0.5 mm in diameter, were made of the stock bismuth. Since the principal susceptibilities of a single crystal of this material had been determined, the susceptibility for a polycrystalline was calculable.

A film of thickness about 0.001μ was now deposited and a number of the extruded wires, of the same length as the film, were tacked down upon this film with drops of collodion so as to form an artificial "film" of known susceptibility. The magnetic forces on the 0.001μ evaporated film were, of course, negligible in comparison with those on the wires. The film merely marked the proper location for the latter.

Results

In Fig. 2 a curve has been plotted showing the diamagnetic susceptibility as a function of film thickness, and, for comparison, the susceptibility of a single crystal (dotted line) placed in the field (H) with [111] parallel to H, and therefore perpendicular to the axis of the crystal rod. In passing we may mention that the single crystal value is determined from a crystal grown from

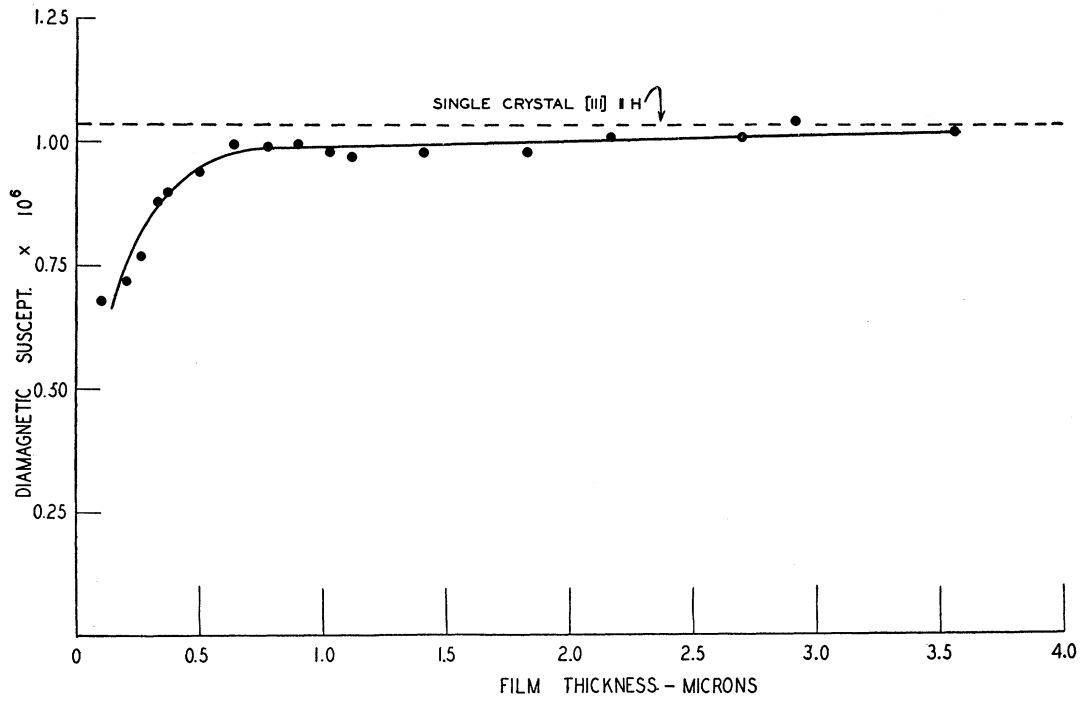

FIG. 2. Curve showing the relation between susceptibility and film thickness.

the same stock material as was used to produce the films, at a fast rate of speed (4 mm per minute) in order to insure that any possible impurities present in the stock material would be distributed uniformly throughout the resulting crystal.

It will be noticed that for thicknesses from about 0.5μ upwards the susceptibility is practically independent of the film thickness and very close to the value for a single crystal for the orientation mentioned above. It is true that the curve does rise somewhat in this region apparently approaching the single crystal value more closely as the film becomes thicker. However, the effect is small and it is rather doubtful whether the accuracy of the experiment is sufficient to warrant a definite conclusion on this point. Below 0.5μ, however, and down to 0.1μ, where the method begins to be seriously inaccurate, the susceptibility definitely decreases as the film thickness is reduced. It may also be mentioned that the susceptibility in this region is smaller than that which is found in massive Bi whether mono- or polycrystalline.

In order to study the effect of the rate of deposition on the structure of the deposits, a number of films of approximately the same thickness (1μ) but produced by widely different rates of evaporation were studied. It was found that the rate of deposition, within wide limits, (30 to 3000 seconds for deposit) had no effect upon the susceptibility nor, by inference, upon film structure.

The effect of the backing substance on the film structure was also investigated. To do this a thick film ($>10\mu$) of another metal was deposited by evaporation on the glass and on top of this layer was condensed the Bi film, the susceptibility of which was to be found. The backing layer was of course compensated by a similar layer on the other glass. No significant difference could be detected in the susceptibility of Bi when deposited respectively on glass, gold, copper and tin. Since glass is amorphous, gold and copper cubic, and tin tetragonal, the structure of the Bi layer is, to this extent, at least, independent of the backing material. Indeed it was found possible to deposit a visible layer of gold on top of the Bi film without appreciably destroying the structure of the film as judged by its suscep-

tibility. The effect of aging the films was also tried. For those thicker than 0.5μ no effect was observed when the films were left in high vacuum for many hours at room temperature. For films below this thickness, however, it was found that the absolute value of the susceptibility tended to increase and approach that of a thick film, especially for films about 0.1μ thick. A similar effect has been found for the electrical resistivity and it is reasonably ascribed to a recrystallization process.

The presence of gas H_2 in amounts from 0.01 to 0.001 mm was found to produce a considerable effect on the structure of the films. The effect of poor vacuum tended to be somewhat irregular but roughly speaking the more gas was present the more nearly the film tended to behave like a random polycrystalline aggregate. In order to study this effect more closely the dependence of the susceptibility on the angle between the film normal and the magnetic field was measured. The results of this are shown in Fig. 3, the notation being such that at zero degrees abscissa the film normal is parallel to the field. Curve D is for a film approximately 2μ thick produced in high vacuum (at between 10^{-5} and 10^{-6} mm Hg). This film possessed a parallel susceptibility (i.e., film normal parallel to H) of $x_{\parallel}=1\times10^{-6}$ and an anisotropy $x_{\perp}/x_{\parallel}=1.33$. These are fairly close to the values for a single crystal with [111] parallel to H (dotted curve C, $x_{\perp}/x_{\parallel}=1.404$). It must be noticed here that in order to make measurements on the susceptibility at 90° to the normal it was obviously necessary to employ a wide air-gap, with a corresponding reduction in the magnetic field strength and in the sensitivity. As a consequence, the accuracy of the points plotted at either side of the figure is least. Curve B is that for a film produced with a residual pressure of hydrogen of about 10^{-3} mm of Hg. It will be seen that this curve departs from the single crystal type much more noticeably. The anisotropy is now reduced to 1.25, and, what is more important, the relatively accurately determined parallel susceptibility has increased to 1.17×10^{-6}.

Curve A is that for a film produced with a still higher pressure of gas in the chamber. This film is apparently a random polycrystal, its susceptibility, 1.30×10^{-6}, being close to the suceptibility of the polycrystalline bulk metal (1.33×10^{-6}).

Discussion

Before proceeding with a review of the results obtained in this work it is in order to make some comparison with previous results. As far as the writer is aware the only other determination of the susceptibility of a nonferromagnetic film is the author's own work[7] published in 1932. This experiment differed in two important respects from the present one. First, no absolute measurement of the susceptibility was attempted; the ratio of the susceptibilities of presumably comparable films was measured. Second, the arrangement of the apparatus was such that the film normal was always perpendicular to the magnetic field. Again the measurements were carried out in vacuum and the thickness of a film could only be rather roughly estimated from the time of exposure to the molecular beam under standard conditions. These experiments showed that, within an estimated error of 10–15 percent, no difference in the perpendicular susceptibility occurred between thicknesses of 0.2μ film and 15μ.

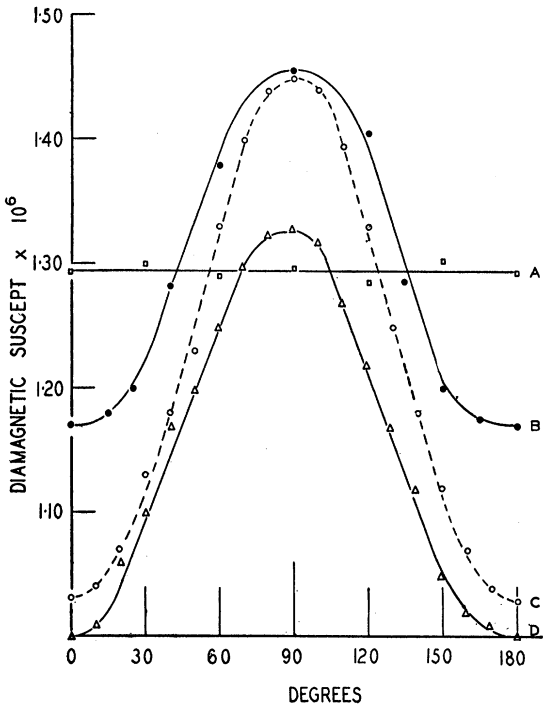

FIG. 3. Curves showing the relation between susceptibility and angle between film normal and magnetic field for various films.

[7] C. T. Lane, Nature **130**, 999 (1932).

From what has been said it is clear that no direct comparison can be made with the present experiments. However, it seems strange that the perpendicular susceptibility, $x_\perp$, should behave so differently from the parallel susceptibility, $x_{\parallel}$. Referring to Fig. 2, however, it is seen that, for the perpendicular setting, the susceptibility of a film 0.3μ thick differs from that for a 3μ film by only 18 percent which is not far from the possible experimental error in the earlier work. Further we now know that thin films tend to increase susceptibility when left in high vacuum. Hence some legitimate doubt may be cast on the validity of the earlier work, although as has been emphasized, no direct comparison is possible. The accuracy of the present work should be about 3–4 percent.

That the effect found cannot be ascribed to impurities in the original bismuth metal is apparent when we consider the anisotropy ratio $(x_\perp/x_{\parallel})$ of the single crystal. For our material this ratio, which of course can be measured with great accuracy, turns out to be 1.404 as against 1.406 by Goetz *et al.* and 1.393 by Schoenberg.[8] As Goetz and his co-workers have shown, this ratio is very sensitive to impurities. We must conclude therefore that the rise in susceptibility shown by films less than about 0.5μ is due to a transition from a microcyrstalline to a macrocrystalline structure, completed at about this thickness. As has been mentioned the dependence of susceptibility on particle size seems to be well established experimentally, at least for graphite and bismuth, although the theoretical reasons for this are still somewhat osbcure.[9] Again since the susceptibility for films below 0.5μ is less than the smallest value ever obtained in bulk material $(x_{\parallel})$ it is most likely that the fiber structure with (111) parallel to the surface of deposition is maintained as we pass through the transition point. This, of course, is in agreement with the electron diffraction experiments. The work is in disagreement with Goetz, Stierstadt and Focke as to the thickness of the microcrystalline layer by a factor of about 200. The writer feels that purely microscopical observations have to be interpreted with very great care if dependable conclusions are to be reached.

With regard to the effect of gas in the apparatus curve B in Fig. 3 is of special interest. It may readily be shown that the apparent susceptibility x for a monocrystal rod is given by

$$x = x_\perp \sin^2\theta + (x_\perp \cos^2\phi + x_{\parallel} \sin^2\phi)\cos^2\theta,$$

where in θ, and ϕ are, respectively, the angles between the trigonal axis and the magnetic field and between the trigonal axis and the (axial) direction of the measured force. For the single crystal (curve C) we have $\phi = 90°$. If now in a film $\phi < 90°$, the perpendicular susceptibility ($\theta = 90°$) will be the same as before; the pseudo-parallel susceptibility ($\theta = 0$) will, however, be greater than previously found for the single crystal. Thus the presence of approximately 10^{-3} mm of gas in the apparatus disturbs the normal crystalline growth of the films. The trigonal axis of the crystallites composing the film are not now accurately perpendicular to the surface of deposition but rather scatter about the normal to this surface. The presence of still more gas in the apparatus tends to accentuate this effect until a pressure is finally reached wherein the crystal structure of the film is "destroyed," i.e., the film is now composed of crystallites orientated at random with respect to the backing surface (curve A).

In conclusion I should like to express my gratitude to Professor L. W. McKeehan for his interest in this work and also to Dr. A. B. Focke of Brown University for his generous gift of some single crystal bismuth seeds.

[8] Cf. reference 4, page 125.

[9] The effect has recently been found for quartz. Y. Shimizu and N. Takatori, Sci. Rep. Tohoku Imperial Univ., Honda Anniversary Volume, p. 306 (1936).