graph. The agreement of the results by the present method with those of Grossmann, obtained by a direct method, is interesting and seems to give considerable support to the validity of interferometric methods in this range of frequencies. The magnitude of A at the maximum at 98 kc/sec. for CO_2 is considerably greater than that of Grossmann and is still farther from the theoretical value.[6] The values of A for air and helium are of a smaller order of magnitude and are much more affected by the errors of measurement.

Reflection coefficients have been plotted as a function of frequency in Fig. 3. It was found by Hubbard that reflection coefficients in this frequency range are less than unity by much more than would be expected on the dynamical theory of sound. The present experiments show that this decrease from expected values is not only very considerable but that the reflection coefficients decrease rapidly with increasing frequency. No detailed explanation of this phenomenon has been attempted, but it seems reasonable to suppose that the same increase with frequency of temperature gradient in the acoustic wave which accounts for the increase with frequency of acoustic absorption due to heat conduction[9] may also be the cause of irreversible heat losses at the reflector. On this view it would be reasonable to expect a decrease of reflection coefficients with increasing frequency.

The author wishes to express his thanks to Professor J. C. Hubbard for suggesting the problem and for much help and encouragement in its solution.

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[9] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).

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Electrical Resistivities of Single and Optically Mosaic Zinc Crystals

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The Voigt-Thomson symmetry relation is accurately checked for two sets of strain-free zinc single crystals made from two lots of Evanwall zinc. The principal electrical resistivities in micro-ohms/cm^3 are: $\rho_0=6.218$, $\rho_{90}=5.882$ with the ratio, $\rho_0/\rho_{90}=1.0554$ for one lot (E.W.R.) and $\rho_0=6.161$, $\rho_{90}=5.842$, $\rho_0/\rho_{90}=1.0548$ for the other (E.W.B.). The resistivity is changed by slight strains due to application of micrometer calipers to the crystals, the change being a decrease in four cases out of eleven. Severe strains, in general, increase the resistivity. The effects of repeated anneals on strained crystals are complex, the most important conclusion being that high temperature anneals (at about 400°C) are not effective in restoring the initial resistivity of all orientations. A final low temperature anneal (at 190°C for 84 hours) is however completely effective. Optically mosaic specimens have abnormal resistivities, either greater or less than single crystals of the same orientation. Such specimens are very strain-sensitive, the resistivity rising markedly after a strain and falling for a subsequent anneal. This effect may be repeated several times on a specimen. The ambiguous results of previous observers may be explained either as strain effects or as due to the presence of optically mosaic specimens.

INTRODUCTION

THE necessity for a redetermination of the resistivity of single crystal castings of zinc as a function of orientation,[1] in spite of several previous determinations,[2] will be evident upon reading the paper on this subject by Tyndall and Hoyem.[2f] None of the previous determinations have really offered a complete and definite experimental check of the Voigt-Thomson symmetry relation[3] for the resistivity when all of the

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[1] The angle between the main crystallographic axis and the length of the specimen.

[2] a. Grüneisen and Goens, Zeits. f. Physik **26**, 235 (1924); b. P. W. Bridgman, Proc. Am. Acad. Sci. **60**, 305 (1925); c. P. W. Bridgman, Proc. Am. Acad. Sci. **61**, 101 (1928); d. P. W. Bridgman, Proc. Am. Acad. Sci. **63**, 352 (1928); e. L. A. Ware, Phys. Rev. **35**, 989 (1930); f. Tyndall and Hoyem, Phys. Rev. **38**, 820 (1931); g. Goens and Grüneisen, Ann. d. Physik **14**, 164 (1932).

[3] This well-known relation states that the resistivity of zinc crystals is a linear function of the square of the cosine of the orientation.

crystals on which measurements were made are considered. The most comprehensive sets of data are those of Bridgman and Tyndall and Hoyem.

Bridgman's latest data[2d] are considerably scattered, but the Voigt-Thomson relation appears to be satisfied by a straight line drawn through the lowest points on his plot, the scattering of points above the line being supposedly due to strains incurred before measuring the crystals. The ratio of principal resistivities, ρ_0/ρ_{90}, is 1.039 for the line drawn as just described. Tyndall and Hoyem used two brands of zinc, for one of which, Kahlbaum's best, was obtained a satisfactory[4] confirmation of the symmetry relation with a ratio, ρ_0/ρ_{90}, equal to 1.057. The second lot of zinc, New Jersey Zinc Company's "spectroscopically pure"[5] (S. P.) showed much the same type of scattering of observations as that of Bridgman. The writers, however, interpret these data to give the same value of ρ_0/ρ_{90} as for the other lot of zinc preferring to believe that the crystals of low resistivity are in some way abnormal.

The writer's purpose in undertaking this investigation was twofold: (1) to obtain an unambiguous check on the Voigt-Thomson relation and a correct value for the ratio, ρ_0/ρ_{90}, with sets of crystals that could certainly be considered free from strain at the time of the measurements, (2) to study the effects of straining and subsequent annealing with the hopes of throwing some light upon the inconsistencies of previous determinations. The writer believes that he has been successful in both points although in the second case an alternative explanation may be given as will appear later.

PRODUCTION OF CRYSTALS

Two sets of single crystals, each distributed throughout the possible orientation range, were grown from two lots of Evanwall 99.99+percent zinc. The material for the first set was part of the same lot of zinc used by Hanson.[6] It will be denoted hereafter as E. W. R.[7] The zinc used for the second set was taken from the same 50 lb. block from which Cinnamon's[8] crystals were grown. It will be denoted hereafter as E. W. B. The two lots of zinc were very similar, the main difference being slight traces of iron in the E. W. R. that were not present in the E. W. B. It may also be of interest to note that both of these lots of zinc were distinctly purer, as shown by spectroscopic analysis, than the Kahlbaum zinc of which the *K* crystals of Tyndall and Hoyem[2f] were grown.

In addition to the truly single crystals a number of "Optically mosaic,"[9] designated hereafter as "O. M.," specimens were grown of both lots of zinc.

All of the crystals were grown in a transite mold in a horizontal furnace by a method similar to that recently described by Cinnamon.[10] The single crystals and O. M. specimens made from E. W. R. zinc were 12 cm long and had a nearly square (actually trapezoidal) cross section of about 1 cm². With the exception of one crystal, they were grown before the inception of Cinnamon's work and his development of the technique of growth.[10] Crystals with orientations between 15° and 50° did not grow the full length of the mold but changed to higher orientations of from 70° to 90° a few centimeters from the neck. This was probably due to an incorrect ratio of the temperature gradient to the rate of growth in the front part of the furnace. Small crystals from various sources were used as nuclei during this part of the work. The first of these were the crystals of Kahlbaum's best zinc grown by Hoyem.[11] In no case did any of these nuclei become O. M. or start O. M. specimens. Later, crystals grown by Schilling,[9] the writer, and others were used. These generally[12] produced

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[4] That is, completely satisfactory to Tyndall and Hoyem, although later Goens and Grüneisen (Ann. d. Physik **14**, 164 (1932)) favor the lower value of ρ_0/ρ_{90}, but their experimental evidence is not very extensive.

[5] This "spectroscopically pure" zinc was some of the material prepared by Cyr, and is not identical with the "spectroscopically pure" zinc now being prepared by the New Jersey Zinc Company.

[6] A. W. Hanson, Phys. Rev. **45**, 325 (1934).

[7] That is, "Evanwall rod," as it was received from the manufacturer in the form of cast rods 1.25 cm in diameter and 25 cm in length.

[8] C. A. Cinnamon, Phys. Rev. **46**, 215 (1934).

[9] H. K. Schilling, Physics **5**, 1 (1934).

[10] C. A. Cinnamon, R. S. I. **5**, 187 (1934).

[11] These are the *K* crystals of A. G. Hoyem, Phys. Rev. **38**, 1357 (1931) and of T and H, reference 2f. Practically all of these crystals were used as nuclei.

[12] In a good many cases O. M. nuclei were deliberately used in order to grow crystals of this type. In many other cases, however, the nucleus appeared to be single and the O. M. structure was started in the portion of the nucleus

O. M. specimens. To finish the set, several of Hoyem's S. P. zinc crystals,[13] particularly those crystals for which the resistivity was lower than normal,[2f] were used as nuclei and a large number of O. M. specimens and a few singles resulted.[14]

The crystals of the second set were grown to the full 12 cm length and with a cross-sectional area of 1.1 cm². Cinnamon's growing apparatus was used and his conditions of growth were satisfied. The long stem on the mold which he used to prevent the formation of an O. M. specimen was dispensed with, however, and crystals[15] containing about 0.3 percent of cadmium were used as nuclei. Without an exception, these nuclei started single crystals, and whenever Cinnamon's conditions were fulfilled, the original orientation would grow throughout the entire length of the casting. It may be noted that the writer found, as predicted by Cinnamon,[10] indications of an upper limit for the region of successful growth. The data were not extensive enough to set a definite boundary line for all orientations, but it seems probable that the region of successful growth is narrow for crystals of 35° orientation, and broadens out for both lower and higher orientations.

Spectral analyses of small sections of both ends of a number of crystals from this set were made to see if the nucleus had contaminated the casting with cadmium. No such contamination was detected.

Experimental Procedure

The resistivity was measured immediately after the growth of each crystal by the usual potentiometer method of comparing the potential drop across the specimen with that across a standard resistance.[16] The potentiometer[17] was made more sensitive by reducing the "working current" of the instrument to approximately one-seventh of its normal value. The current leads to the crystal were battery clips that were shaped to fit exactly the ends of the casting. The potential contacts were steel needle points[18] passing through holes in a Bakelite strip and pressed lightly into contact with the crystal by means of small rubber bands, thus assuring good electrical contact without introducing an appreciable strain upon the specimen. Six such contacts, spaced approximately one centimeter apart, were used on the first four crystals grown, so that a correction for the variation of the cross-sectional areas could be made as described by Tyndall and Hoyem.[2f] The later crystals were so nearly uniform in cross section that only the potential drop across the extreme contacts needed to be recorded. During the electrical measurements, the specimen was inserted in a Dewar flask. The temperature of the crystal was determined by the use of thermocouples placed at each end of the section being measured.

After the electrical measurements were taken, the positions of the contacts were measured with a Gaertner comparator. The mean cross-sectional area was then determined by the use of micrometer calipers. The altitude of the trapezoidal shaped cross section was measured with an ordinary micrometer, and the side dimensions were taken with a special pointed type micrometer. Approximately fifty micrometer readings on five separate sections of the specimen between the potential contacts were recorded to determine the mean area. To obtain consistent results for the altitudes of the five sections, the jaws of the micrometer were closed quite firmly upon the casting, undoubtedly introducing strain. Hence, after the micrometer measurements, the specimens were considered as strained crystals. The specific resistance for each crystal at room temperature (23°–31°) was computed and reduced to 20°C by using a temperature coefficient, α, equal to 4.058×10^{-3} per degree centigrade.[19]

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that was melted and recrystallized, as described by Cinnamon, reference 10.

[13] A. G. Hoyem, Phys. Rev. **38**, 1357 (1931).

[14] These crystals were used as nuclei to test whether they were single or O. M., it being believed, at the time that this was done, that single crystal nuclei would start single crystals and O. M. would start O. M. specimens. This test did not prove conclusive since it is now known that either single or O. M. may come from a single crystal nucleus.

[15] Grown by Professor E. P. T. Tyndall by the Czochralski-Gomperz method.

[16] The same standard resistance that was used by Tyndall and Hoyem. It was recently checked against a new standard resistance, and found to agree with its stated value (0.01 ohm) within seven parts in ten thousand.

[17] For the first set of crystals investigated, a type *K* Leeds and Northrup potentiometer was used, but for the second set, it was replaced by a more sensitive instrument, type K_2.

[18] Phonograph needles.

[19] The value found by Hoyem (Phys. Rev. **38**, 1357 (1931)) for the S. P. zinc. It was checked by the writer for the E. W. B. zinc.

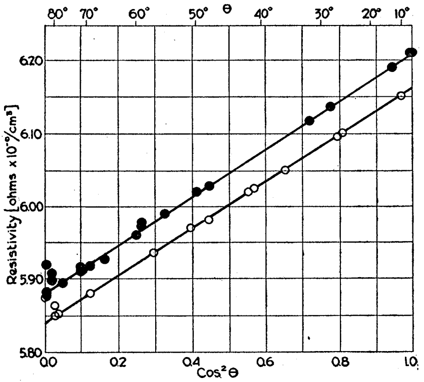

FIG. 1. Resistivity of strain-free crystals. Closed circles (●), E. W. R. zinc; open circles (○) E. W. B.

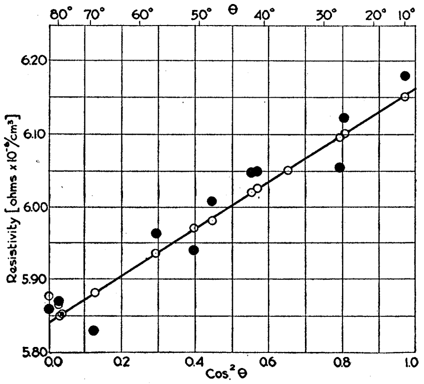

FIG. 2. Effect of a slight strain produced by micrometers shown by closed circles (●), E. W. B. zinc.

RESULTS AND DISCUSSION

Resistivity of single crystals

The initial resistivities of the single crystals of both sets are shown in Fig. 1 as a function of the square of the cosine of the angle of orientation. Except for a few crystals between 80° and 90°, a consistent and definite check on the Voigt-Thomson symmetry relation is obtained. The ratio of the principal resistivities, ρ_0/ρ_{90}, is 1.0554 for one set (E. W. R.) and 1.0548 for the other (E. W. B.), the difference appearing real although not very much greater than the experimental error. The difference in resistivity of the two lots of zinc is definite and in such a direction as to indicate a greater purity for the E. W. B. If this is due to its apparent freedom from iron, the effect of small amounts of iron on the resistivity of zinc must be very great. As the two sets were grown and measured under somewhat different conditions, an additional crystal of E. W. R. was grown and measured under precisely the same conditions as that of the E. W. B. crystals after the work on the latter was completed. This crystal ($\cos^2\theta = 0.72$, $\rho = 6.117$) agreed perfectly with the other crystals of the same set, the point for it falling on the upper line in Fig. 1.

The complexity of the effect of impurities may perhaps be brought out by noting that the results for the E. W. R. zinc are in exceedingly close agreement with the K zinc of Tyndall and Hoyem.[2f] Thus for E. W. R. $\rho_0 = 6.218$, $\rho_{90} = 5.882 \times 10^{-6}$ ohm/cm³; for the K zinc[20] $\rho_0 = 6.217$, $\rho_{90} = 5.884 \times 10^{-6}$ ohm/cm³. Yet the E. W. R. zinc undoubtedly contains less cadmium and lead than the K zinc. Also, the E. W. B., although certainly less pure than the S. P. zinc, agrees very well with it. Thus for E. W. B. the results are: $\rho_0 = 6.161$, $\rho_{90} = 5.842 \times 10^{-6}$ ohm/cm³; for the S. P. zinc,[20] $\rho_0 = 6.182$, $\rho_{90} = 5.847 \times 10^{-6}$ ohm/cm³ these last two values being of course somewhat uncertain on account of the previously mentioned scattering of results of the S. P. crystals. Results of the above type may be taken to show that there is some small amount of impurity by which the resistivity of zinc is very critically affected. Such a conclusion, however, is to be regarded as largely speculative until supported by further evidence.

It seems to the writer that the question of the ratio of the two principal resistivities of zinc crystals must be considered as definitely settled, the value lying somewhere between 1.054 and 1.057, slightly different ratios being perhaps possible for different lots of zinc.

The ratio of principal electrical resistivities, 1.0548 (at 20°C) for the E. W. B. zinc is in such close agreement with Cinnamon's[8] ratio of principal thermal resistivities, 1.0588 (at 57°C), that his conclusion of the constancy of the Wiedemann-Franz ratio for all orientations is now fully confirmed by electrical and thermal measurements made on crystals of the same zinc. Cinnamon's value of the W–F ratio (at 57°C) must be

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[20] Tyndall and Hoyem determined the cross sections of their crystals by weighing a measured length and using a density of 7.15 g/cm³. The values quoted above are corrected to a density of 7.13 g/cm³ which the writer determined for a single crystal of E. W. R. zinc.

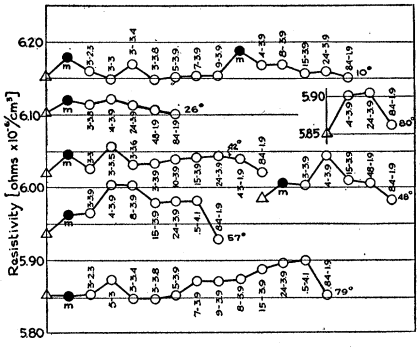

FIG. 3.

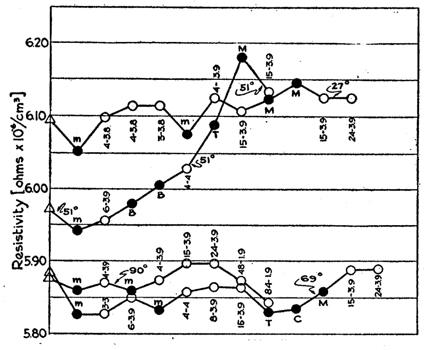

FIG. 4.

FIGS. 3 AND 4. Effects of strains, subsequent anneals, etc. Triangles (△), initial unstrained resistivity. Closed circles (●), resistivity after a strain designated by letters near points, as follows: *m*, a slight strain produced by micrometers; *M*, severe strains produced by micrometers; *B*, bent and straightened; *T*, twisted 1° per cm length; *C*, compressed in a vise. Open circles (○), values after an anneal indicated in hours and hundreds of degrees C.

decreased by about 0.6 percent due account being taken of the difference in resistivity and temperature coefficient of the E. W. B. zinc and *K* zinc, the electrical properties of the latter having been used by Cinnamon in computing his Wiedemann-Franz ratio.

Effect of strains, subsequent anneals, etc., on the E. W. B. single crystals

Special care was taken, in the previous work, not to strain the crystals before making the electrical measurements. To test particularly the possibility of strain occurring during the necessary manipulation, several of the E. W. B. crystals were carefully removed from the holder, replaced and remeasured. This second measurement of resistivity agreed with the first in each case to about one part in three thousand. After application of the micrometers, however, a definite change of resistivity occurred as shown by the closed circles in Fig. 2. In four cases distributed throughout the range of orientations, the micrometer strains lowered the resistivity.[21] Hence, a strain does not necessarily produce an increase in the resistivity as heretofore supposed. While this fact appears adequate to account for some of the abnormally low resistivities found in previous investigations, it is necessary before accepting such an explanation to prove that the previous specimens were not only strained when measured but were definitely "strain-sensitive"[22] in the same way as the writer's crystals.

After the crystals had been strained by the micrometer measurements, some of them were subjected to various anneals and in some cases to further strains between anneals. These results are given graphically in Figs. 3 and 4. The triangles represent initial values of resistivity, the closed circles values of resistivity after a strain, the nature of which is indicated by the small letter near the point (see Fig. title). The open circles show the resistivities after anneals, the duration and temperature (hours —degree C/100) being indicated beside each measurement. While the phenomena appear complex certain salient features may be pointed out. After the first strain, which in every case was due to micrometer measurements, a subsequent anneal returned the resistivity towards its initial value irrespective of whether the strained value was high (Fig. 3) or lower (Fig. 4). A second micrometer strain produced the same effect as the first, even though many hours of annealing had intervened. Severe strains

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[21] An attempt was made to find some correlation between the orientation of the lattice with respect to the direction of the stress produced by the micrometers. For instance, if a stress nearly parallel to the cleavage planes produced an increase in resistivity, the opposite effect might be expected for a stress perpendicular to the cleavage planes; also the inclination between the stress and one of the minor crystallographic axes might be significant. No obvious correlations of this sort were discovered. In one case, two crystals that behaved oppositely were grown from the same nucleus and had practically identical orientations of the lattice ($\theta = 26°$ and $27°$, Fig. 2). To pursue this point further the stress would have to be more definitely controlled.

[22] That is zincs with more or different impurities might behave differently.

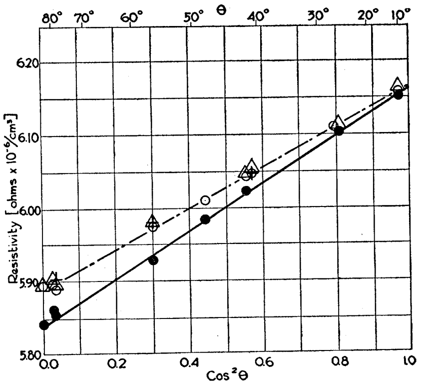

FIG. 5.

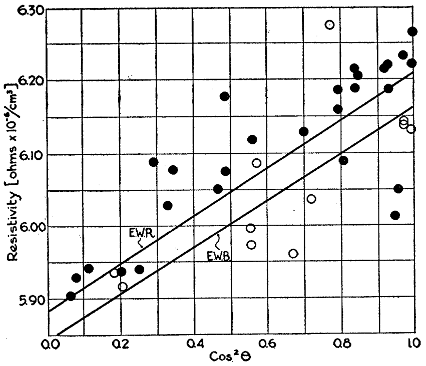

FIG. 6.

FIG. 5. Comparison of high and low temperature anneals for slightly strained crystals. Open circles (○), after an anneal of 15 hours at 390°C and all previous anneals as shown in Figs. 3 and 4; triangles (△), additional 24 hours at 390°C; crosses (+) additional 0.5 hour at 415°C; closed circles (●), after a final anneal of 84 hours at 190°C.

FIG. 6. Resistivity of optically mosaic specimens. Closed circles (●), E. W. R. zinc; open circles (○), E. W. B.

(*B*, *T*, *M*) with one exception (*T* on 69° crystal Fig. 4) produced increases in resistivity. Anneals for longer times and at successively higher temperatures in general caused increases in resistivity except for crystals of low orientation. A final long anneal at a low temperature (190°), however, restored the slightly strained crystals to initial values. The effect of the last few anneals is shown somewhat differently in Fig. 5. A definite equilibrium condition appears to be reached for an anneal of 15 hours[23] at 390°C,[24] open circles, subsequent anneals, longer (triangles) or higher (crosses) producing no marked effect. All these points lie rather smoothly upon a line above the normal line, the departure from the normal being proportional to $\sin^2\theta$. The final anneal of 84 hrs. at 190°C on eight of the crystals distributed throughout the orientation range is shown by the closed circles. The solid line represents the normal resistivities (lower line in Fig. 1). The effectiveness of this low temperature anneal in restoring the normal resistivities is very striking, particularly after the failure of the high temperature anneals. The case of the 90° crystal is particularly interesting in that this anneal lowered the resistivity to the line determined by the other single crystals in spite of the fact that its initial resistivity was higher than normal.

After this restoration to initial resistivities the crystals appeared far more strain-sensitive than they were just after growth since it was found that very slight handling again increased the resistivity.

Optically mosaic specimens

The initial resistivities for both sets of O. M. specimens are shown in Fig. 6. The points are considerably scattered. In the case of the E. W. B. zinc, the majority of the points fall below the line for the corresponding single crystals. Except for the accidental bending of two specimens, 29° (E. W. B.) and 45° (E. W. R.), all were handled as carefully as the single crystals. In view of the strain effects previously described for single crystals, it seems probable that the initial, and usually abnormal, resistivities of O. M. specimens are due to strains incurred during the growth process, particularly during the slow cooling after solidification since the elements of the O. M. structure are not of precisely the same orientation and would contract differently. Depending upon the amount and character of the strain, abnormally low as well as abnormally high resistivities are to be expected. It is obvious, moreover, that such specimens cannot be expected to adhere to the Voigt-Thomson symmetry relation.

After the results just described were obtained, it seemed very probable that the scattering of

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[23] This does not include the time required to heat and cool the crystal.

[24] The difference in temperature between the two ends of the specimen was less than 3°C.

results found by Tyndall and Hoyem[2f] for the S. P. crystals could be explained by assuming that some of those crystals were O. M. and not single. A re-examination by Professor Tyndall of the remaining fragments confirmed this hypothesis, some O. M.'s being found but not of very pronounced types. They consisted mainly of occasional "mosaic patches" near the edges of the cleavage planes, or double crystals of nearly the same orientation. It is not possible to ascertain definitely now just how many of the crystals were O. M. but the presence of only a few is sufficient to account for the results of Tyndall and Hoyem. It is interesting to note that several other properties of these crystals which were investigated by Hoyem[13] showed no abnormality, O. M. specimens apparently behaving like single crystals.

Whether the scattered results of other workers can be explained by the presence of mosaics cannot be asserted, but it is apparent that such results can be duplicated by the use of a mixed set of O. M. and single crystals.

The O. M. specimens showed very marked and characteristic effects due to repeated successive strains and anneals. Typical results are shown in Fig. 7 in which is plotted for each specimen the difference $(\rho - \rho_n)$ between its resistivity and the normal resistivity (i.e., that of a single crystal of the same orientation) against the state of the specimen as shown by the letters along the axes of the abscissae. The effect of a pronounced strain, whether bending or twisting, is to raise the resistivity. A following anneal always lowers it, occasionally to values even below the normal value. There is no apparent correlation between the types of O. M., as classified by Schilling,[9] and the magnitude of the effect produced by certain strains or anneals.

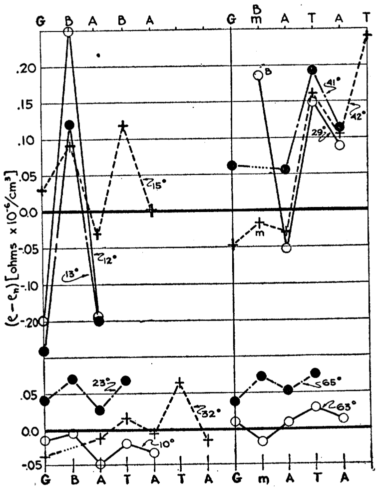

FIG. 7. Effect of successive strains and anneals on optically mosaic specimens. *G*, as grown; *A*, after anneal; *m*, after a slight strain produced by micrometers; *T*, after a twist of 1° per cm length; *B*, after bending and straightening.

Practically all of the anneals for these specimens were at low temperatures and for short periods of time, usually at 200°C for 5 hours. None of the strains were severe enough to produce visible strain bands on the surface of the specimens. None of the specimens recrystallize on heating. An attempt to recrystallize a slightly strained O. M. specimen into a single crystal by keeping it at 417°C for one hour was unsuccessful. The O. M. structure looked exactly the same afterwards as before, indicating possibly that the strain was everywhere below the critical strain needed for recrystallization.

In conclusion, the writer wishes to thank Professor E. P. T. Tyndall for suggesting the problem, for this helpful criticisms and for his continued interest throughout the investigation.