The Influence of Plastic Deformation on the Superconductivity of Metals

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THE INFLUENCE OF PLASTIC DEFORMATION ON THE SUPERCONDUCTIVITY OF METALS *

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To be determined was the influence of plastic deformation on the superconductivity of tin, indium, thallium, and mercury. It was found that plastic deformation of tin, indium, and thallium causes a marked increase in the critical temperature; however the T_k of mercury remained unchanged under the same conditions. The results obtained were compared with data on the effect of all-sided thorough compression on superconductivity. The possibility of the polymorphic transformation of Thallium II - Thallium III under these conditions is also discussed.

INTRODUCTION

The vast amount of experimental material on the problem of determining the critical parameters of superconductors (the critical temperature T_k, the critical field H_k and the value dH_k/dT) supports the view that physical and chemical impurities in metals have an extremely strong effect on the T_k and dH_k/dT. An analysis of the H_k - T curves shows that in the purest physical and chemical test samples this relation can be expressed for all superconductors by a single universal linear of the type $h = 1 - t$, where $h = H_k/H_{k_0}$ and $t = T^2/T_k^{\ 2}$ (1). It has been observed that the more imperfect the sample is, the greater are the deviations from this rule. Lazarev and Galkin (2) have demonstrated that the superconducting qualities even of such a "classical" superconductor as tin can be altered very significantly by creating large internal stresses in the material. In their experiment a tin wire, which was attached by celluloid glue

*[Note: The figures, 1-17, are in the appendix.]

to a glass plate, had a critical temperature of about 8 degrees K, a dHk/dT equal to 2000 G/degrees and a strongly increased (by 100 times) residual resistance. However, owing to the very complex character of the deformation in the material under these conditions, the results, unfortunately must be interpreted chiefly qualitatively. Therefore, a correct calculation of the effect of the various heterogeneities is very essential. In as much as the combined action of physical and chemical impurities in the material gives complex effects, which are difficult to calculate, it is expedient to separate these items.

To correctly calculate chemical heterogeneities is very difficult since they not only distort the lattice but even can interact with the atoms of the solvent, thus forming alloys and amalgams by changing the electron distribution in the metal. Much better results can be obtained by studying the effect of plastic deformation on superconductivity in material which is chemically very pure, as the source of all possible physical impurities -- distortion of the lattice, alteration of its parameters, formation of the texture, etc.

We tested tin, indium, thallium, and mercury under plastic deformation. (In addition to these metals, tantalum and two superconducting alloys, Sn-Sb and Sn-Zn were studied.) It was found that plastic deformation essentially changed the superconducting qualities of the metals studied, particularly the critical temperature, so that the temperature field extent in the superconductivity of pure metals can be significantly expanded. At this point we shall cite part of the experimental data obtained.

APPARATUS AND TEST SAMPLES

(More detailed information on the apparatus and measuring method are to be found in our article, "Plastic Deformation of Metals at the

Temperature of Liquid Helium," published in the ZhTF.)

The plastic deformation in our tests was accomplished by compressing a cylindrical conductor -- a thin wire 0.08 - 0.3 millimeters in diameter and 18 millimeters long -- between two flat surfaces at different stresses, and consequently, at different degrees of deformation, beginning with an elastic one. The amount of deformation in the material was limited only by the mechanical durability of the apparatus and of the material in the support plates.

In the apparatus, the rotation of a rod through two cogged gears and one worm gear moved the mobile plate, which was pressed to the support plate with a force reaching 4000 kg, so that specific stresses could be built up to 2.10^4 kg/cm^2. The apparatus was placed in a Dewar flask, which was filled with liquid helium, and curves of the temperature and magnetic transitions were taken as the amount of deformation in the test sample was increased. The resistance of the test samples was measured by a small-ohm Dieselhorst compensator, the temperature being determined by vapor tensions of liquid helium in accordance with the 1940 scale. (3).

We shall not stop on the preparation of the test samples but will indicate only that the analytic data, the magnitude of the residual resistance and the steepness of the superconducting transition permit us to conclude that the purity of the test samples was satisfactory and that there were no significant stresses in the original state.

MEASURING METHODS

The change of residual resistance in the test sample was chosen as the criterion for the degree of plastic deformation; the destruction and distortion of the lattice in the metal were used to measure the degree of physical imperfection. The results of the experiments, it seems to us, confirm our choice; and therefore in all our measuring, we used the relationship R_o'/R_o -- where R_o' is the resistance of the test sample at a given temperature when T = 4.2 degrees K and R_o is the residual resistance of the original test sample at the same temperature. For non-distorted material $R_o'/R_o = 1$.

The measuring was carried out in the following fashion. A test sample with current and potential electrodes was placed in a free state between the plates of the apparatus. The apparatus was filled with liquid helium. Then we determined the residual resistance of the original sample, the temperature and the magnetic transition curves. After this, known stress was applied and the measurements were repeated up to the maximum stresses and deformations. The dimensions of the sample were determined at the end of the experiment. We established the magnitude of the final deformation and made an approximate evaluation of the specific stress.

In Figure 1 are shown curves of the residual resistance change in a tin wire of varying diameters, depending on the stress applied.

Figure 1. Tin. 1 -- diameter of wire 0.19 millimeters; 2 -- 0.135 millimeters; 3 -- 0.10 millimeters; 4 -- 0.08 millimeters.

[See figures in appendix]

As was to be expected, the residual resistance of the test sample rose very strongly in the beginning, moving towards saturation as the stress was increased. It is evident from the diagram that there is a perfectly defined change of residual resistance, corresponding to a given strain and that this is different for each diameter of the test sample. Curves for the other metals tested possess the same characteristic.

CHANGE OF SUPERCONDUCTING QUALITIES

1. Tin was tested by us in great detail. An application of the smallest stresses (100 grams) in the fashion already noted tells on the transition curve. (A special press was used for small stresses.) Figure 2 shows the superconducting transition curves of such a sample 0.15 millimeters in diameter with and without stress.

Figure 2. Tin. 0 -- superconducting transition curve of the original sample; 1 -- the same, under stress.

As can be seen from the diagram, applying stress brings about an increase in residual resistance accompanied by such a widening of the superconducting transition interval that the form of the transition curve calls to mind the transition curve for polycrystallized material which has been heterogeneously subjected to strain. Under such stress, the deformation of the test sample is more elastic; taking off the stress practically returns the transition curve to its original position. At the same time, the residual resistance is also decreased, returning to its original value. Further increasing the stress by plastically deforming the test sample brings about a further change of superconducting qualities in the sample. This is plotted in Figure 3.

Figure 3. Tin. Diameter of test sample 0.135 millimeters. 0 -- superconducting transition curve of original test sample; 1 -- the same, at stress of 140 kilograms; 2 -- the same, at stress of 200 kilograms; 3 -- the same at stress of 250 kilograms.

The curves are numbered in order according to the increase in stress. It is evident from Figure 3 that increasing the stress brings about a continuous rise of residual resistance, accompanied by more and more widening of the superconducting transition interval.

Since the relative change of residual resistance is extremely great in large stresses, for the sake of convenience, we will give all further transition curves in coordinates, where R_{usl} represents the relation of the resistance of the material at a given deformation and temperature to its resistance when T = 4.2 degrees K (R_{usl} = 1 for each degree of deformation when T = 4.2 degrees K). Figure 4 illustrates the change of superconducting qualities of this test sample when further increasing the stress up to the maximum.

R_{usl}

R_{usl}

Figure 4. Tin. Diameter of test sample 0.135 millimeters. 0 -- original sample; 1 -- stress of 140 kilograms (R_o'/R_o = 1.8); 2 -- stress of 175 kilograms (R_o'/R_o = 3.1); 3 -- stress of 200 kilograms (R_o'/R_o) = 4.25); 4 -- stress of 250 kilograms (R_o'/R_o=5.6); 5 -- stress of 260 kilograms (R_o'/R_o = 6.6); 6 -- stress of 360 kilograms (R_o'/R_o = 9.6); 7 -- stress of 620 kilograms (R_o'/R_o = 14.0)

At the outset, an increase in ~~stress~~ brings about a rise in critical temperature of the superconducting transition, until the relationship R_o'/R_o which determines -- as has already been pointed out -- the degree of plastic deformation, reaches a value of 7. At this point the critical temperature starts to go down again, reaching the T_k value of the original sample.

It must be mentioned in connection with the ever widening interval of superconducting transition that the usual definition of T_k as the temperature in which the resistance of the material is equal to one-half the residual is not as valuable in the given experiments as considering T_k to be the temperature in which the material begins to possess superconducting qualities; i.e., when superconductivity, caused by plastic deformation of the material, occurs.

The curves in Figure 5 show the T_k - R_o'/R_o relationships which correspond to the transitions plotted in Figure 4.

Figure 5. Tin. 1 -- T_k reading taken when R_{usl} = 0.05; 2 -- T_k when R_{usl} = 0.50; 3 -- T_k when R_{usl} = 0.95

The T_k values were also read when the R_{usl} was 0.95, 0.50 and 0.05. As can be seen from the figure, all curves are monotypes which flatten off when the R_o'/R_o equals 7. Therefore in further statements we will accept T_k as the temperature when R_{usl} equals 0.5 since this can be determined very accurately; and also, the material begins to have superconducting qualities at a much higher temperature.

We obtained the T_k - R_o'/R_o curves for material of different diameters. They are plotted in Figure 6.

Figure 6. Tin. 1 -- Diameter of material 0.19 millimeters; 2 -- 0.135 millimeters; 3 -- 0.10 millimeters; 4 -- 0.08 millimeters.

It is interesting to note that the height of the maximum depends on the diameter of the test sample, however the position of the maximum on the R_o'/R_o axis is the same for all diameters of the wire, and this confirms the criterion chosen as correct for the degree of plastic deformation in the material. Even a cursory examination of the curves plotted indicate that in the case of plastic deformation the effects observed are completely distinct from phenomena explained by thorough compression (4,5) or tension (6,7). However, the greatest difference is observed when the maximum stress is removed from the test sample (the unnumbered curve in Figure 4). When this occurs, instead of a return to its original position, the transition curve is displaced still further in the high temperature field so that the T_k becomes greater than the T_k of the original material by 0.35 - 0.40 degrees. This displacement is more or less the same in all cases. All these results will be reviewed below in more detail.

Indium behaves exactly like tin under conditions of plastic deformation. Figure 7 shows the variation of the superconducting transition curves with the degree of deformation.

R_{usl}

R_{usl}

Figure 7. Indium. 0 -- original sample

1 - stress less than 50 kg (R_o'/R_o = 3.56)

2 - stress 180 kg (R_o'/R_o = 5.6)

3 - stress 810 kg (R_o'/R_o = 9.1)

4 - stress 1450 kg (R_o'/R_o =10.8)

5 - stress 3040 kg (R_o'/R_o =12.3)

The T_k - R_o'/R_o relation is plotted in Figure 8. Removing the stress (the unnumbered curve in Figure 7) also brings about a further rise in T_k (the diameter of the sample was 0.20 millimeters).

Thallium. Plastic deformation in the case of thallium brings about a continuous rise of the T_k. Only under the greatest stresses reached in our apparatus was saturation observed, (this is presented graphically by the curves in Figures 9 and 10), after which an insignificant decrease of T_k was likely (not shown in Figures 9 and 10).

Figure 9. Thallium. 0 -- original sample; 1 -- stress of 120 kilograms ($R_o'/R_o = 5.5$); 2 -- stress 320 kilograms ($R_o'/R_o = 10.5$); 3 -- stress 620 kilograms ($R_o'/R_o = 16.2$); 4 -- stress 900 kilograms ($R_o'/R_o = 22.0$); 5 -- stress 1530 kilograms ($R_o'/R_o = 34.2$); 6 -- stress 2800 kilograms ($R_o'/R_o = 48$)

Figure 9 shows the fluctuation of the transition curves under the influence of plastic deformation, and Figure 10 shows the change of T_k with R_o'/R_o. Taking off the stress (the unnumbered curve in Figure 9) also is accompanied by a rise of T_k (diameter of the sample was 0.22 millimeters).

Mercury under plastic deformation behaves quite differently from the 3 other superconductors described. When compressing mercury wire, increasing the stress causes a linear displacement of T_k towards low temperatures; that is, an effect occurs which is contrary to that observed in tin, indium and thallium. This is plotted in Figures 11 and 12.

Figure 11. Mercury. Diameter of sample 0.30 millimeters -- original sample; 1 -- stress less than 50 kilograms ($R_o'/R_o = 2.0$); 2 -- stress 180 kilograms ($R_o'/R_o = 4.9$); 3 -- stress 1050 kilograms ($R_o'/R_o = 8.3$); 4 -- stress 2450 kilograms ($R_o'/R_o = 10.8$)

The T_k fluctuated linearly up to the greatest stresses reached by us, after which removing the stress returned the transition curve practically to its original position, close to the transition curve of non-distorted material.

2. The value of dH_k/dT in tin, indium and mercury under plastic deformation changes rather insignificantly; it increases slightly as the degree of deformation is increased. An exception to this is thallium, whose dH_k/dT under deformation increases strongly, reaching a value of 500 G/degrees and more; whereas the original material has a $dH_k dT$ equal to 150 G/degrees. Along with this, the width of the transition interval of these samples (especially of thallium) increased a hundred times, reaching a value of a score or two gausses.

3. All these effects are observed only when deformation takes place at a low temperature (in our experiment 4.2 degrees K). When the material is heated at room temperature all the abnormalities of superconductivity disappear, and when cooled again, the material has practically normal residual resistance, normal T_k and normal superconducting transition interval width. If deformation of the material (tin) takes place at 77 degrees K, abnormalities of superconducting qualities are observed, although fewer of them are brought about than by deformation when $T = 4.2$ degrees K. Deformation at room temperature practically does not change the superconducting qualities in "soft" superconductors, whose recrystallization temperature is close to room temperature or in tantalum, for which recrystallization sets in when T is more than 1000 degrees C. (Regarding this, it has now become clear that impurities and not deformation are the basic reason for the abnormal superconducting qualities of tantalum.)

DISCUSSION OF RESULTS

The general picture of the relation of the critical temperature to the degree of plastic deformation of the metals tested is presented by the graph in Figure 13. Along the ordinate axis is plotted the relative displacement of the critical temperature T_k'/T_k for each metal; on the abscissa R_o'/R_o.

It is natural to wish to correlate the results obtained with data on the influence of thorough compression on superconductivity (4,5). From this point of view, it is simplest to treat the results obtained for mercury. In reality, compression of the material produces a lowering of the critical temperature just the same as under conditions of thorough compression (10), and removing the stress brings about a return of the transition curve to its original position. Mercury is very plastic at low temperatures (11), and since the maximum stress in our measurements was about 3000 kilograms, the material was absolutely distorted into thin leaf, which according to the data of Bridgeman should practically be thorough compression under these conditions. Unfortunately, because the material melted when heated, it was difficult to determine the specific stress; however these results do correspond qualitatively to data on the thorough compression of mercury.

On the other hand, a very different picture is observed for the plastic deformation of thallium. According to extant data, thorough compression of thallium brings about a lowering of the T_k (13). Thus the continuous rise of T_k in thallium as the stress is increased agrees with this information. However, removing the stress unexpectedly brings about a still further rise of the T_k at a time when the compressing forces are not present.

Not less surprising from this point of view is the behaviour of tin and indium. Thorough compression of these metals brings about a lowering of the T_k (4,5). At the same time, as seen in the curves, the change of T_k in their plastic deformation is described by a curve which flattens off at the top. Removing the compressing forces from the material results in raising the T_k in both materials.

Since the method of distorting all these four metals is exactly the same, such a great difference in their behaviour is evidently to be explained by deeper causes. Considering that mercury behaves just as it is supposed to on compression, all the observed abnormalities can be easily explained if it is supposed that plastic deformation of Sn, In and Tl transforms these metals into a somewhat different state, which is characterized by an increase of the critical temperature. In this case, this is the T_k which plastically distorted material has after the stress has been removed. The effect of lowering the T_k, caused by thorough compression is superimposed on to the effect of raising the critical temperature. Since the T_k of the distorted material has a definite value and the lowering of the T_k due to compression increases as the stress is increased, it is natural that the general picture of T_k change in relation to the degree of deformation will be described by a curve which flattens off at the top, just as in tin and indium. This is also confirmed by the curves in Figure 14 which show the variation of T_k in a tin sample 0.16 millimeters in diameter under plastic deformation with stress alternately applied (lower curve) and removed (upper curve).

Figure 14. Tin. 0 -- original sample; 1 -- stress 120 kilograms; 3 -- stress 180 kilograms; 5 -- stress 250 kilograms; 7 -- stress 320 kilograms; 9 -- stress 520 kilograms; 2, 4, 6, 8, and 10 without stress.

The numbers on the points of the curves correspond to the sequence of the measurements.

In order to put the data for thallium into this scheme, it is necessary to assume that plastic deformation of thallium has a normal sign dT_k/dP just as tin and indium do. In Figure 15 are shown curves of the T_k change in a thallium wire 0.22 millimeters in diameter under plastic deformation with stress alternately applied and removed (symbols are the same as in Figure 14).

Figure 15. Thallium. 0 -- original sample; 1 -- stress 120 kilograms; 3 -- stress 270 kilograms; 5 -- stress 720 kilograms; 7 -- stress 1280 kilograms; 9 -- stress 1780 kilograms; 11 -- stress 2250 kilograms; 2, 4, 6, 8, 10 and 12 without stress.

A glance at the diagram shows that when the R_o'/R_o is more than 12, the dT_k/dP has a normal sign; that is, applying the stress lowers the critical temperature. Thus, the maximum in the lower curve in Figure 15, which depends on lowering the T_k as a result of thorough compression, has to be developed at much greater stresses than for tin or indium.

Tests were also made on the compression of very thin lamina of tin, indium and thalium when it was thought that thorough compression was probably taking place. Without going into details of the experiments, we will indicate only that in all these metals, compression under such conditions produces an effect with a normal sign; that is, applying stress lowers the critical temperature.

It is known that plastic deformation of metal at low temperature, especially in combination with thorough compression, can bring about polymorphic transformation. Barrett (14) reports on phase transition in lithium under plastic deformation when T = 77 degrees, and the newly formed phase (a face-centered cube $a_0 = 4.41\mathring{A}$) is stable only up to a temperature of 156 degrees K. [Note: The text has a typographical error at this point. The text has the phrase "phase transition v linii" (in line) whereas it should be "phase transition v litii" (in lithium).]

Bridgeman (12) points out the existence of polymorphic transformation in a whole series of metals, including the transition Tl II - Tl III, which takes place when T = 170 degrees K and $P = 4.3 \cdot 10^4$ kg/cm^2. He indicates the possibility of such a transformation in tin when P is more than $5 \cdot 10^4$ kg/cm^2.

Now we do not have available information which would indicate that the observed effects are the results of similar polymorphic transformation; however, such a probability seems well founded to us, especially for thallium, if the sign change dT_k/dP and the large change of dH_k/dT is taken into consideration.

In any event, it is evident that all these metals being plastically distorted at low temperature are found in a somewhat metastable state, caused by the presence of irregular distortion of the lattice and variation of its parameters. In regard to this, the observed effect of the T_k increase is expressed not only by widening the transition interval as could be expected in a physically contaminated superconductor, but also in the displacement of the whole transition curve towards high temperatures. A somewhat indirect indication which must be viewed simply as an accumulation of physical impurities in the material is the fact that the width of the superconducting transition interval, which characterizes the homogeneity of the material in tin, indium and thallium, reaches a maximum; whereas in mercury -- where these effects are absent -- the interval width continuously increases. In Figure 16, is shown a curve of the relation of interval widths to the degree of deformation for tin, and in Figure 17 the same is given for mercury. Here T_1 and T_2 are beginning and ending temperatures of the superconducting transition read at points where R_{usl} equalled 0.95 and 0.05.

CONCLUSIONS

1. Plastic deformation of tin, indium and thallium at low temperature brings about the formation of a somewhat metastable state, which is characterized by an increase in value of the critical temperature.

2. The presence of a peak in curves showing the relation of critical temperature to the degree of plastic deformation in the metals enumerated is caused by superimposing the influence of all-sided thorough compression, which lowers the T_k, on to this effect.

3. An examination of these results leads to the conclusion that under the conditions of our experiment, the transformation of Tl II - Tl III, observed by Bridgeman, could have occurred.

4. The observed effects which are caused by low temperature do not occur if the deformation takes place at higher temperatures even though lower than the temperature of recrystallization.

5. Plastic deformation of mercury is not accompanied by similar effects. The lowering of T_k observed is caused by all-sided thorough compression.

Further research in this direction will be conducted.

In conclusion, we thank Professor B. G. Lazarev for his constant attention to our work and for giving us a series of valuable suggestions, and also Professor I. V. Obreimov and Professor B. Ya. Pines for discussing and evaluating our results.

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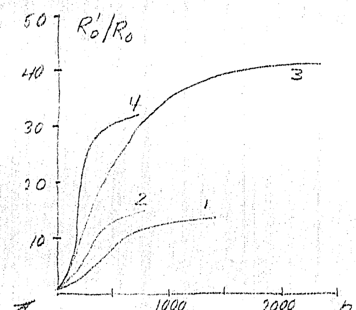
[Figures 1 - 17 follow]

FIGURES 1- 17



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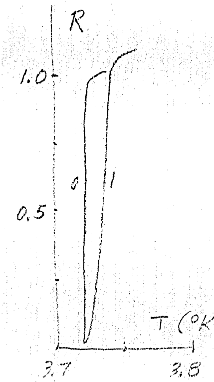

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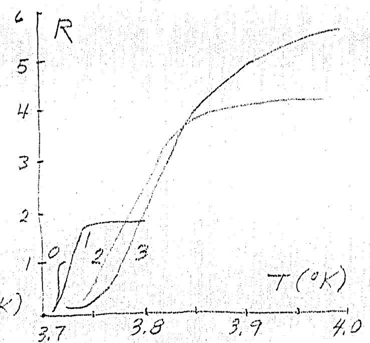

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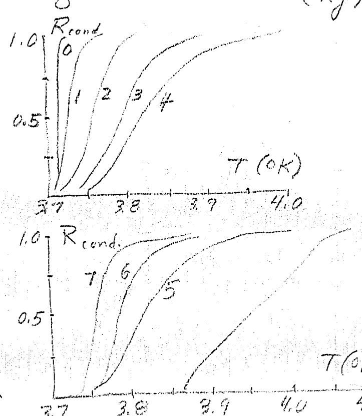

Figure 4

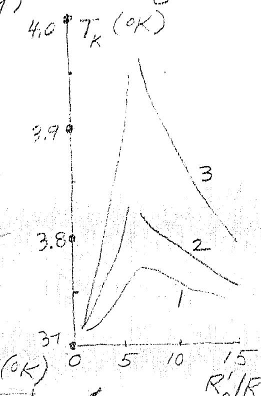

Figure 5

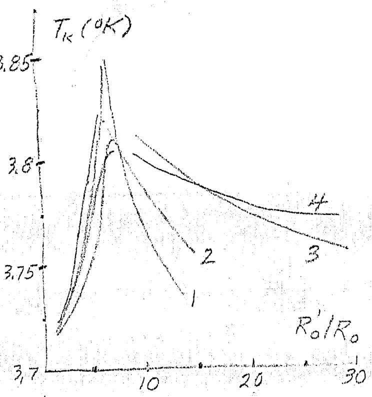

Figure 6

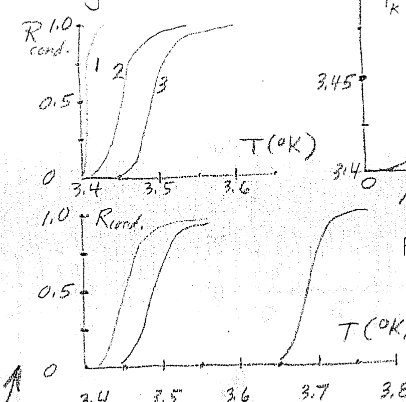

Figure 7.

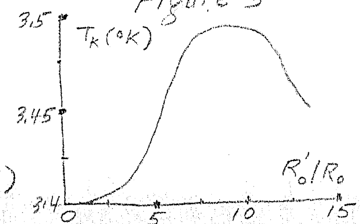

Figure 8.

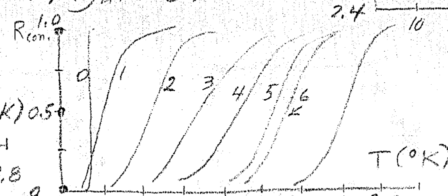

Fig. 9

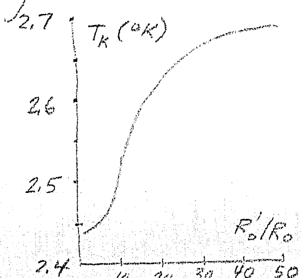

Figure 10.

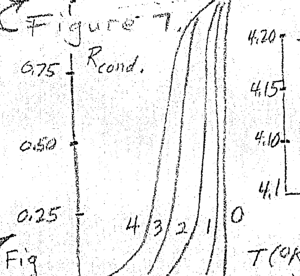

Fig 11.

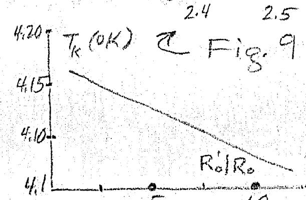

Fig. 12.

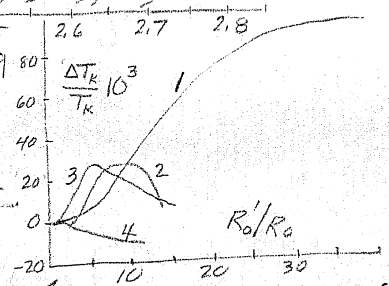

Figure 13.

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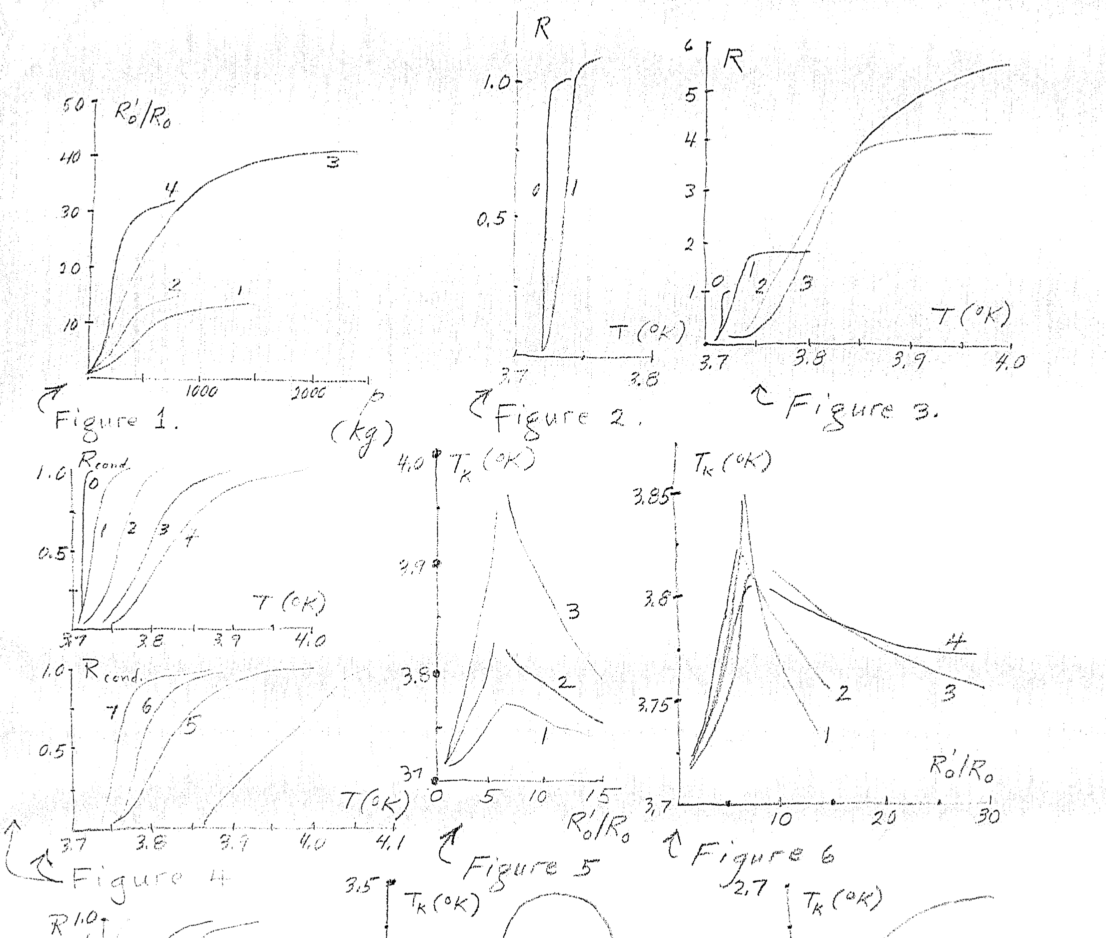
FIGURES 1- 17



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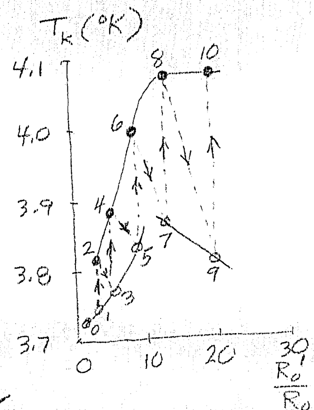

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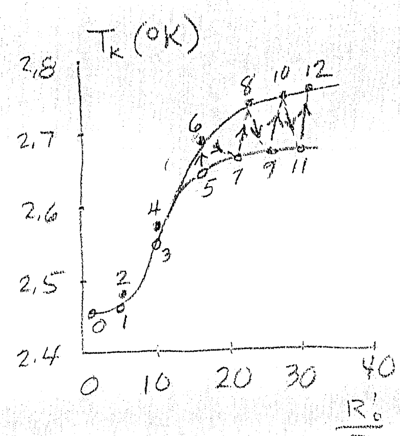

Figure 15.

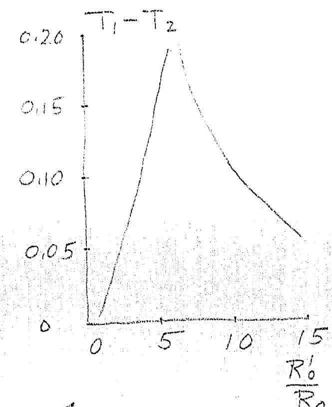

Figure 16.

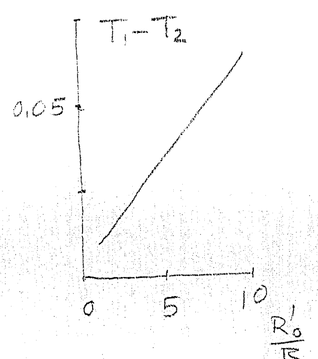

Figure 17.

– END –

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