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Structure of the Intermediate State in Superconducting Lead

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The Faraday effect in a cerous nitrate-glycerol mixture has been employed to study the structure of the intermediate state. A lead alloy containing antimony and tin was used as a specimen, and behavior characteristic of the hard superconductors was observed. Photographs were taken showing the distribution of normal and superconducting material at various magnetic fields. The configurations observed are briefly discussed in terms of current theories of the intermediate state.

INTRODUCTION

A NUMBER of techniques have been employed to render visible the distribution of magnetic field at the surface of a superconductor in the intermediate state. Meshkovsky and Shalnikov[1] employed the magnetoresistance of a fine bismuth probe to map the domains on the flat surface of a tin hemisphere. More recently, Schawlow[2] published the results of work done using superconducting niobium powder sprinkled on the surface of disks of several superconducting metals, notably tin. Very well-defined domain patterns emerged and were photographed and strong differences in pattern type were observed, depending on the metal being studied. The work reported here has employed still another phenomenon, the Faraday effect, for the observation of the intermediate state.

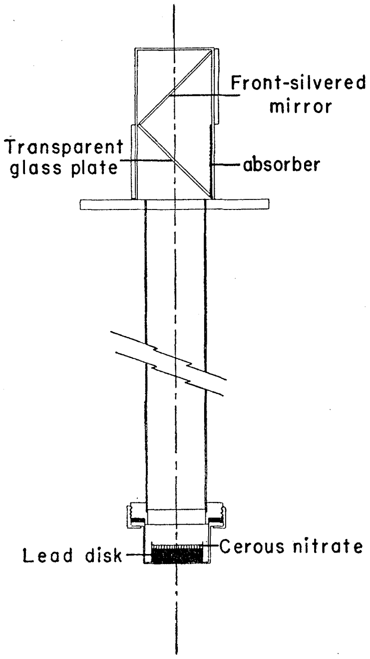

FIG. 1. Diagram of experimental apparatus.

The Faraday effect is the rotation of the plane of polarization of a light beam when it is passed through a magnetized substance in the direction of the applied field. It was used extensively by Becquerel and coworkers[3] to study the properties of many paramagnetic substances at low temperatures, and the rotations observed, especially in the cerium (Ce^{+++}) salts, were considerable. The amount of rotation is proportional to the magnetization of the salt, and for most paramagnetic substances, the magnetization is essentially proportional to the applied field for low fields (<1000 gauss).

It would seem, therefore, that if a thin layer of a paramagnetic substance were placed on a superconductor in the intermediate state it would be magnetized over the areas of normal metal and unmagnetized over the superconducting areas. If polarized light traveling parallel to the applied field were then allowed to pass through the paramagnetic material, the magnetized portions would produce Faraday rotations while the unmagnetized ones would not. Since these rotations are doubled, not cancelled, when the light is reflected back through the substance, the light reflected from superconducting areas would have a different plane of polarization from that reflected from normal areas, and such differences could be seen by means of an analyzer.

APPARATUS

The paramagnetic compound employed was a solution of cerous nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) in glycerol. Cerous nitrate is not a highly colored compound, as are the more common chromium and iron salts, and it is very soluble, so that highly concentrated solutions could be obtained. Glycerol was used as a solvent because it hardens to a glassy transparent solid as it is cooled. The material used in the work reported here was made by dissolving 65 grams of cerous nitrate in 18 grams of glycerol. At 1.8°K this mixture had a rotary power of about (0.5°/mm)/100 gauss.

The superconductor itself was a lead alloy disk $\frac{3}{8}$ inch thick and $1\frac{3}{4}$ inches in diameter. A spectrochemical analysis was made and a quantitative analysis for tin

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[1] A. G. Meshkovsky and A. I. Shalnikov, J. Phys. (U.S.S.R.) 11, 1 (1947); also A. G. Meshkovsky, J. Exptl. Theoret. Phys. (U.S.S.R.) 19, 1 (1949).

[2] A. L. Schawlow, Phys. Rev. 101, 573 (1956).

[3] J. Becquerel and W. J. de Haas, Leiden Comm. 20, Suppl. 74a (1933); also Becquerel, de Haas, and van den Handel, Physica 1, 383 (1934).

TABLE I. Results of spectrographic and quantitative analyses of material of lead alloy disk. Adjectives refer to strength of lines observed in spectrum.

Metal	Pb	Sb	Sn	Cu	Ag	Bi	Fe	Si	As	Mg
Spec. anal.	Very strong	Strong	Strong	Medium strong	Medium	Weak medium	Weak	Weak	Very weak	Trace
Quan. anal.	96%	3½%	¼%			¼%				

and antimony was also run. The results appear in Table I. The presence of these alloying constituents is believed to be responsible for the behavior that was observed.

One face of the disk was given a uniform but not necessarily shiny finish and then was aluminized. A paper rim was glued around this face of the disk and in the cup thus formed the cerous nitrate solution was poured to a depth of about three millimeters. This cup was placed at the bottom of a closed tube as shown in Fig. 1. At the upper end of the tube a beam of monochromatic (5461 A) light passed through a polarizer and was reflected down the tube by an unsilvered glass plate. The light passed through the solution and was reflected back to the top of the tube by the aluminized surface. A front-silvered mirror above the glass plate intercepted the returning light and reflected it to an analyzing polaroid.

The apparatus was constructed so that the tube could be exhausted and the lower end cooled to liquid helium temperatures by means of the conventional arrangement of Dewar flasks. An external set of Helmholtz coils was used to provide the necessary magnetic fields.

Experimental Results

At the beginning of a run, the helium bath was pumped to a low temperature (~1.8°K). This gave a double advantage: the critical field necessary for the suppression of superconductivity reached a high value, and the sensitivity of the cerous nitrate was considerably increased, since the paramagnetic susceptibility is inversely proportional to the temperature. Both conditions serve to improve the contrast between normal and superconducting regions. During this cooling process, the applied field was zero, so the lead disk was completely superconducting at the beginning of any given run. The analyzing polaroid was then set to cancel the light reflected from the disk, and throughout the experiments an area of darkness could thus be taken to indicate superconducting material.

It was found that the field necessary to suppress superconductivity in this particular lead alloy specimen was nearly 1000 gauss. We therefore define $h=H/H_c$ as the ratio of the applied field to the critical field, with H_c taken as 1000 gauss. In addition, Fig. 2 shows a schematic hysteresis loop for which the abscissa is the field ratio h and the ordinate is an average of the fields existing at the surface of the disk, h_{surf}. The diagram is not intended to be quantitative; the points represent the places in the magnetic cycle where the pictures described below were taken.

When the field was slowly increased from zero, no change was observed in the disk until $h\simeq+0.5$. At this point the outer edges of the disk brightened, and as the field increased further, the normal (bright) area increased. Its typical appearance is shown in Fig. 3, for $H=+0.73$. The white circle was drawn to denote the outer edge of the disk, and the fine web-like structure is due to cracks in the cerium-glycerol mixture. Both features are common to all the pictures that follow. It can be seen that the form of the normal ring is similar to the coarse behavior observed by Schawlow in the hard superconductors and the fine radial spoke pattern he observed in tin is apparently not present. The field was increased until 1000 gauss was reached and all superconductivity was quenched.

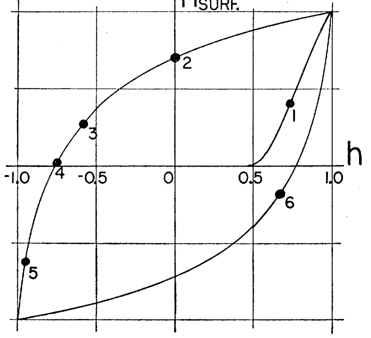

FIG. 2. Schematic hysteresis loop showing points on magnetic cycle where pictures were made. Abscissa is applied field, ordinate is average field at surface of specimen. Both fields are expressed in terms of $h=H/H_c$.

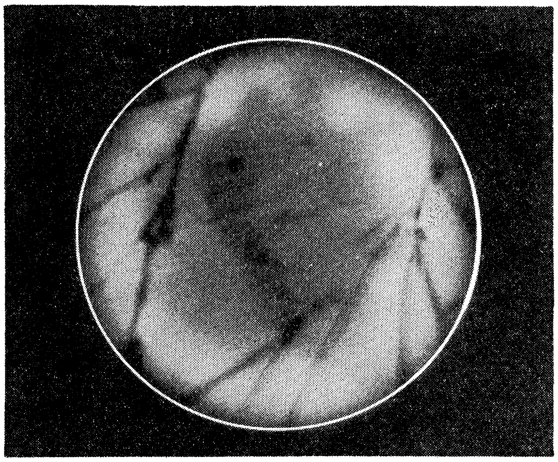

FIG. 3. Intermediate state in lead alloy. Normal areas light. Field penetrating around edges of disk. $T=1.8$°K, $h=+0.73$.

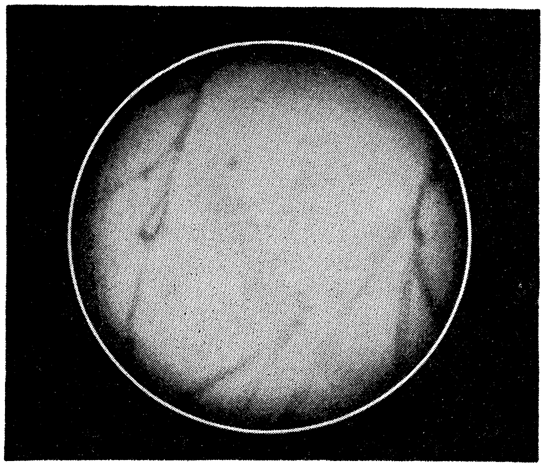

FIG. 4. Intermediate state in lead alloy. Normal areas light. Field frozen-in as H returns to zero. $T=1.8°\text{K}$, $h=0$.

The field was then reduced to zero. In Fig. 4, for $h=0$, we can see that a considerable amount of flux has been trapped. Less clearly, a ring of superconducting material can be seen lying just inside the edge of the disk, and a faint shadow indicates the presence of a small amount of superconducting material within the ring. Such a strong frozen-in field is another characteristic of the hard superconductors. In this case, such behavior is probably due to the alloy nature of the specimen, since preliminary experiments on a disk of pure polycrystalline lead indicate little or no hysteresis effects.

At this point, the current leads to the Helmholtz coils were reversed and the field was increased in the opposite direction. The peripheral ring of superconducting material continued to grow inward until the field at the edge of the disk exceeded the critical field again. The resulting configuration is shown, for $h=-0.61$, in Fig. 5. The center of the disk remains bright, although the small superconducting inclusions have grown slightly. An apparently continuous ring of superconducting material surrounds the center and a ring of normal material lies around the edge of the disk. This outer ring is dim, showing that the applied field, in addition to being opposite in direction to the frozen-in field, is also smaller. It should be mentioned at this point that no obvious relaxation effects were observed at any time—the patterns changed as the field changed and remained stable indefinitely when the field was held constant. This was probably due partly to the polycrystalline impure material we were using, and also to the fact that no large abrupt changes in field were made. As the field continued to increase, the superconducting ring was compressed until channels began to appear across its center. See Fig. 6 ($h=-0.80$). Finally, the entire superconducting region was reduced to a star-like configuration containing small normal inclusions; Fig. 7, $h=-0.92$.

FIG. 5. Intermediate state in lead alloy. Normal areas light. Applied field around edge, frozen-in field in center. $T=1.8°\text{K}$, $h=-0.61$.

Again the field was reduced to zero. The outer edge of the disk became superconducting and the center figure expanded somewhat. The Helmholtz coil leads were again reversed and the field increased. As before, the outer superconducting border grew inward toward a slightly expanding center. After the edge of the disk was driven normal by the increasing field, the superconducting ring came in contact with the inner figure to produce the striking configuration shown in Fig. 8, for which $h=+0.74$. In this figure the three concentric bright areas represent a complicated field distribution. The field in the center of the star is parallel to the applied field and the field trapped between the star and its circular frame is antiparallel.

The cycle could be repeated indefinitely, and a variety of patterns could be generated. It was also possible to determine the magnitude and direction of the frozen-in fields by rotating the analyzer. While this was not done systematically, it was observed that the fields were quite uniform within the boundaries that confined them. At the boundaries themselves a slight bunching could be observed, but this was taken to be due to a small Meissner effect.

DISCUSSION

The discussion of observations such as these can only be qualitative; however, certain conclusions can be drawn.

It was mentioned above that recent preliminary observations on samples of pure polycrystalline lead showed little or no hysteresis. The specimens we photographed were also polycrystalline but contained substantial alloying material. They exhibited strong hysteresis effects and had a markedly higher critical field than that of pure lead. In addition, the configuration of the boundary between normal and superconducting material, especially on the virgin curve, resembled the boundaries observed by Schawlow in his specimens of tantalum and vanadium. This seems to give support to the belief that the peculiar behavior of the hard superconductors is due more to the phsyical and chemical condition of the specimen under study than to any properties pertaining to the metal itself.

In connection with this, it is felt that while no very well-defined domain pattern emerged in these experiments, the domain picture suggested by Lifshitz and Sharvin[4] is not necessarily negated. In their discussion of the intermediate state, Lifshitz and Sharvin dealt of course with ideal homogeneous material. It is highly probable, however, that in specimens such as those examined here the chemical and physical coarseness present has a profound effect on domain size. Such conditions probably also prevail in such hard superconductors as tantalum, most specimens of which usually consist of many fine grains sintered together.

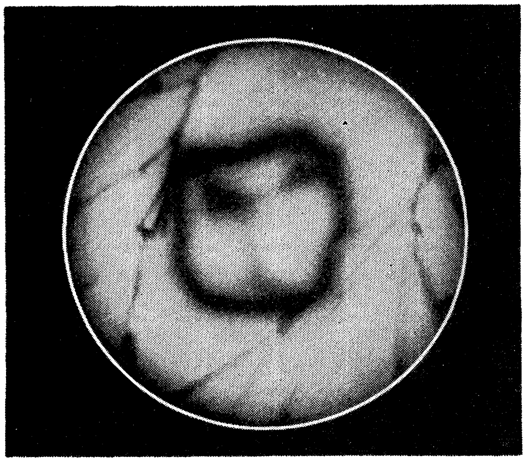

FIG. 6. Intermediate state in lead alloy. Normal areas light. Center area breaking up into "domains." $T=1.8°\mathrm{K}$, $h=-0.80$.

The idea of a grainy superconductor also provides an explanation for the fact that the flux trapped within a ring of superconducting material, as in Fig. 6, has no visible channel of escape. In particular, the picture of the intermediate state proposed by Faber and Pippard[5] would demand this. If, however, we consider the superconducting rings we observe to be composed of many tiny superconducting islands, the ability of the flux to escape becomes a simple matter. The optical resolution of this Faraday technique is such that a single channel could probably be easily seen, since it would doubtless grow, but the many small channels existing in an island structure would remain invisible.

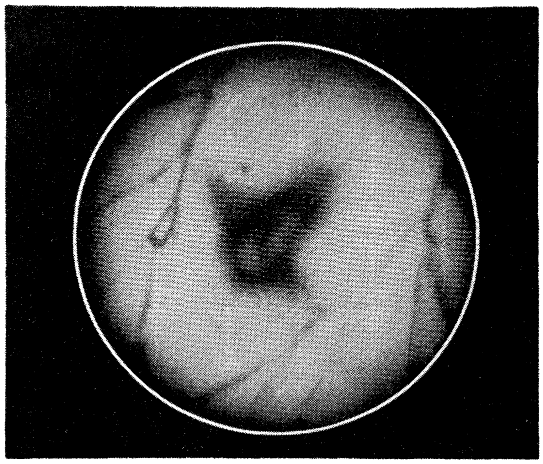

FIG. 7. Intermediate state in lead alloy. Normal areas light. Star configuration in center contains small normal inclusions. $T=1.8°\mathrm{K}$, $h=-0.92$.

CONCLUSIONS

The use of the Faraday effect to render magnetic fields visible, given certain geometric conditions, has drawbacks as well as advantages.

For studies of the intermediate state, the fields involved are relatively small and the paramagnetic compound employed must be correspondingly sensitive. At the moment, the method seems confined to studying the superconductors having high critical fields: lead, some superconducting alloys, and the hard superconductors like tantalum, vanadium, and niobium.

The chief value of the method, however, lies in its application to the study of time-dependent phenomena. A problem of current interest in superconductivity involving transient behavior is the so-called paramagnetic effect.[6] It has been suggested by H. Meissner

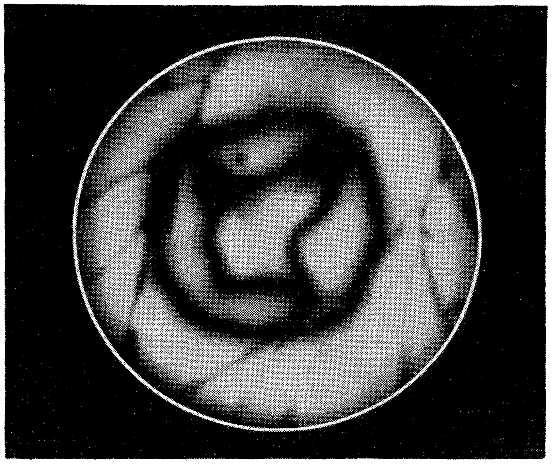

FIG. 8. Intermediate state in lead alloy. Normal areas light. Configuration after applied field removed, then applied in opposite direction. $T=1.8°\mathrm{K}$, $h=+0.74$.

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[4] E. M. Lifshitz and Yu. V. Sharvin, Doklady Akad. Nauk U.S.S.R. **79**, 783 (1951).

[5] T. E. Faber and A. B. Pippard, *Progress in Low-Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1955), Vol. 1, p. 159.

[6] H. Meissner, Phys. Rev. **97**, 1627 (1955); **101**, 31 (1956); and **101**, 1660 (1956). Also J. C. Thomson, Phys. Rev. **102**, 1004 (1956).

that in a superconducting rod carrying a current in a longitudinal magnetic field, a solenoidal current configuration is set up when the metal is in the intermediate state. The collapse of this solenoid when the metal goes normal is thought to be the cause of a sharp paramagnetic peak observed in the magnetic moment. A visual examination of the field changes at the end of such a rod when the rod is driven normal could provide some useful data. In particular, the results should have a bearing on the question of whether the paramagnetic effect is indeed a fundamental property of the superconducting state or due to a peculiar current configuration dependent on geometry.

Another application not involving superconductivity might be found in studies of ferromagnetic domains and the motion of the domain walls in alternating fields.

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Calculation of the Band Structure of "Complex" Crystals

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A method for studying the band structure of "complex" crystals (i.e., crystals having more than one atom per unit cell) is developed. This method is a generalization of one proposed independently and arrived at by different approaches by Korringa and Kohn and Rostoker for the study of the band structure of "simple" crystals. The general approach leads to a promising method when the crystalline potential can reasonably be approximated by a potential which is spherically symmetric within nonoverlapping spheres about the lattice sites and is constant elsewhere. Important virtues of the method are its expected accuracy and the fact that the largest part of the labor involved is in the computation of certain "structure constants" which are applicable to all crystals with the same crystallographic structure.

I. INTRODUCTION

Of basic importance to the theoretical study of the solid state is the knowledge of the nature of the electronic energy bands in a perfect crystal. Consequently, a great deal of effort has been put into devising various techniques for solving the Schrödinger equation with a periodic potential, and in applying these techniques to particular crystals. The problem of determining the band structure of "complex"[1] crystals has presented a particularly formidable computational roblem.

This note will be concerned with the problem of determining the band structure of "complex" crystals. In view of the rather great amount of work encountered in carrying out a calculation for these crystals, it is highly desirable to establish a method that is at once accurate and that does not involve an excessive amount of computational labor. A means of accomplishing the latter aim would be a method in which a large part of the computation is independent of the potential and hence is applicable to all crystals with the same structure. In this way the labor involved in studying the band structure of each individual crystal, or of a particular crystal with each of a number of assumed potentials, is considerably reduced.

For the case of a "simple" lattice, such a method has been developed independently by Korringa[2] and Kohn and Rostoker.[3,*] Korringa approached the problem by considering the scattering of the electron wave by all the atoms in the crystal using an analysis analogous to that employed by Ewald in his study of the diffraction of x-rays by crystals. Kohn and Rostoker, on the other hand, proceeded by establishing a variational principle based on the integral equation for the electron wave function. Both approaches lead to practical results when the crystalline potential can be approximated by a potential which is spherically symmetric within nonoverlapping spheres (henceforth called "atomic" spheres) centered at the lattice sites and constant elsewhere.

The virtues of the method make it apparent that it would be highly desirable to have a method of the type described for the study of "complex" lattices. It is felt that there are many such crystals, particularly those having two atoms per unit cell, for which the abovementioned approximating potential would be appropriate. The difference between the actual crystalline potential and a judiciously chosen approximating potential could then be handled by perturbation theory. With this in mind, we have generalized both the Korringa and Kohn-Rostoker approaches so that the schemes would encompass the more general class of crystals which contain an arbitrary finite number of atoms per unit cell.

The general approach has several important virtues. It has the advantage of the cellular method in that the approximate solutions one works with are solutions of

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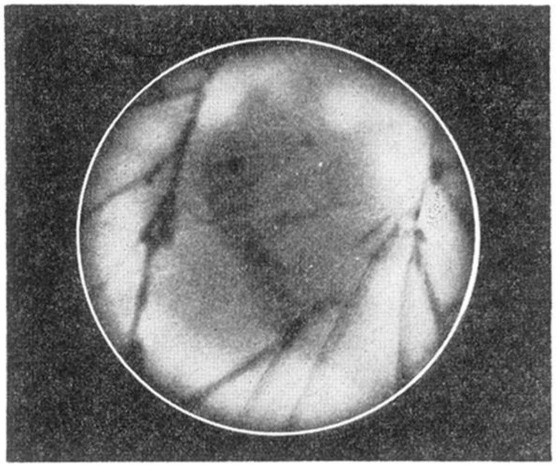
[1] In the following, we shall use the term "complex" crystal (or structure) to mean a crystal with more than one atom per unit cell. Similarly, the adjective "simple" will imply one atom per unit cell.

[2] J. Korringa, Physica 13, 392 (1947).

[3] W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).

[*] P. M. Morse, Proc. Natl. Acad. Sci. U. S. 42, 276 (1956).



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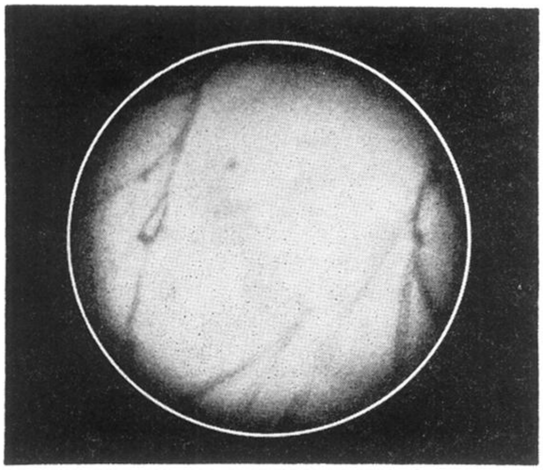
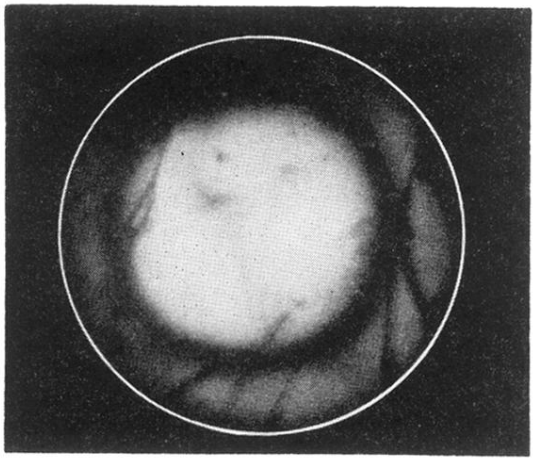


FIG. 4. Intermediate state in lead alloy. Normal areas light. Field frozen-in as H returns to zero. $T=1.8$°K, $h=0$.



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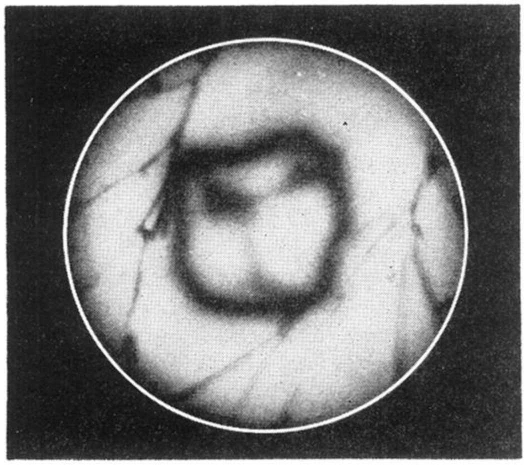

FIG. 6. Intermediate state in lead alloy. Normal areas light. Center area breaking up into "domains." $T=1.8^{\circ}\mathrm{K}$, $h=-0.80$.

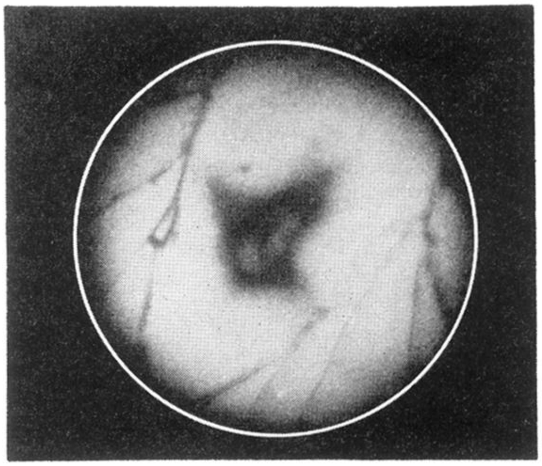

FIG. 7. Intermediate state in lead alloy. Normal areas light. Star configuration in center contains small normal inclusions. $T = 1.8°\text{K}$, $h = -0.92$.

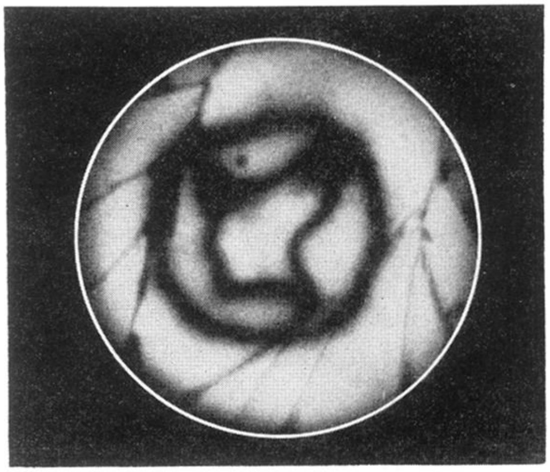

FIG. 8. Intermediate state in lead alloy. Normal areas light. Configuration after applied field removed, then applied in opposite direction. $T=1.8°\mathrm{K}$, $h=+0.74$.