FILAMENTARY STRUCTURE IN SUPERCONDUCTORS

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We have studied the zero-field transitions in a number of superconductors by means of the complex ac susceptibility, and have observed evidence in some cases for the development and growth of a physical filamentary or Mendelssohn sponge network as the temperature is decreased. Because this method gives more complete information than do the conventional ballistic flux and dc resistance measurements, and because the frequency is available as an additional parameter, the method can furnish insights into the nature of the transition not available with the other techniques.

The method consists of measuring the real and imaginary parts of the magnetic susceptibility of a cylindrical sample in a weak alternating magnetic field (~0.04 oersted) as the temperature is lowered through the transition. We find that the temperature variation of the imaginary component follows one of two characteristic patterns. One of these appears to be intrinsically associated with ordinary bulk superconductors and the other with superconductors having a filamentary superstructure.

The interpretation of the data may best be understood by first considering the behavior of the complex susceptibility of a normal metal as a function of conductivity and frequency. The case of a cylindrical rod in an alternating magnetic field is a standard problem.[1] The solution for χ, the complex susceptibility, is

$$\chi = \chi' + i\chi'' = -(1/2\pi)[1 - (2/ak)J_1(ka)/J_0(ka)],$$

where a is the cylinder radius, $k = (1+i)/\delta$, and δ is the skin depth. In Fig. 1, both χ' and χ'' are plotted against a/δ. The maximum in χ'' and the point of inflection in χ' occur when $a/\delta \simeq 1.8$.

In order to exhibit the difference in the character of the transitions for filamentary and nonfilamentary structures, χ'' should not have passed through the maximum in the normal state. For a good conductor such as pure tin, when the conductivity is 1000 times the room-temperature value, the skin depth at a frequency of 25 cps is of the order of a millimeter. However, by using fine wires and low frequencies the required condition, $a/\delta < 1.8$, can be met. With poorer conductors, such as alloy materials, this condition is much easier to fulfill.

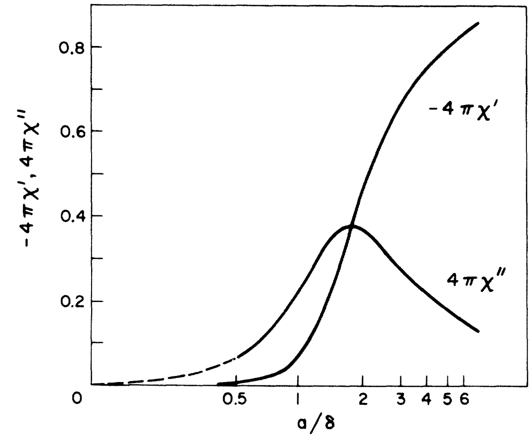

FIG. 1. $4\pi\chi'$ and $4\pi\chi''$ as functions of a/δ for a normal conductor. Longitudinal ac field.

When the sample subsequently goes through the superconducting transition, χ' always changes monotonically, going from a small value in the normal state to $-1/4\pi$ in the superconducting state. For an ordinary nonfilamentary superconductor, χ'' also changes monotonically and goes from its level in the normal state to substantially zero in the superconducting state. Figure 2(a) illustrates such a transition observed with some 99.999% extruded tin wire. The other type of transition, which we submit is characteristic of filamentary structures, is illustrated in Fig. 2(b), which is data taken on a 99.9% cold-worked tin rod. In this χ' changes monotonically as before, but χ'' exhibits a maximum suggestive of that of Fig. 1. Such a broad maximum, which is not characteristic of a homogeneous superconducting material,[2] must be due to a structure which comprises superconducting inclusions in a background matrix of normal conductivity and in this way simulates a homogeneous normal metal on some coarse-grained scale. The maximum in χ'' is essentially the result of two competing mechanisms as in the case of the homogeneous normal metal. The initial appearance of superconducting inclusions increases the average current density[3] (the average electric field intensity remaining constant to a first approximation because the flux density is unchanged), resulting in increased dissipation and hence increased χ''. As the temperature is

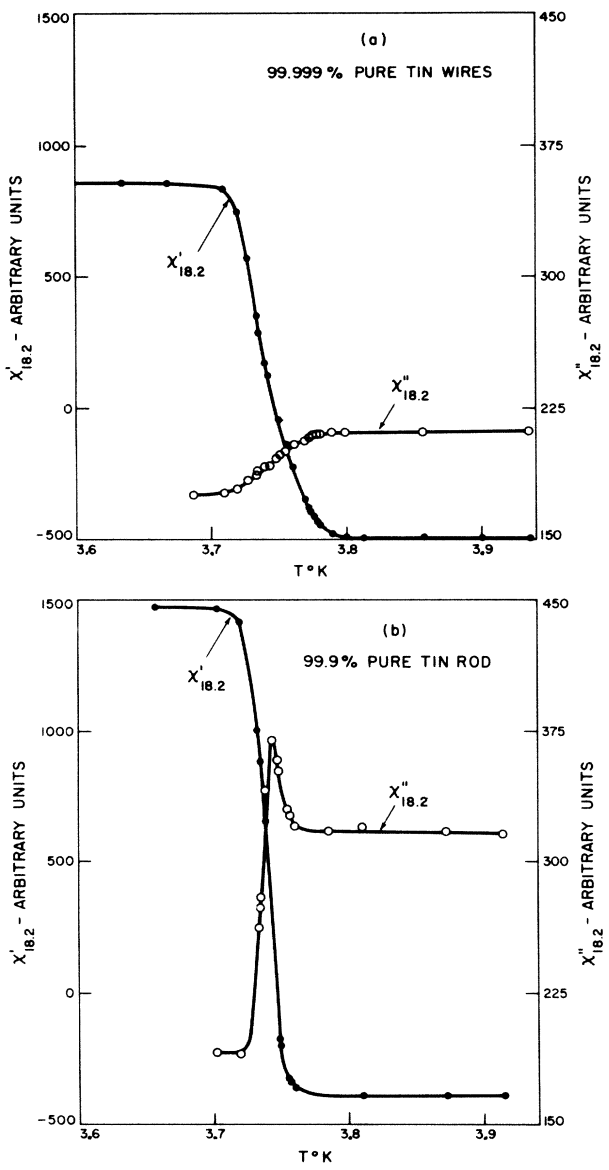

FIG. 2. (a) χ' and χ'' at 18.2 cps for a bundle of 27 extruded tin wires, 0.0125-in. diameter. Batch purity 99.999 %; resistivity ratio of wires ~5000. Both χ' and χ'' are plotted in the same arbitrary units, although the χ'' scale is expanded. Longitudinal ac field. (b) χ' and χ'' for a cold-worked 99.9 % tin rod, resistivity ratio ~300. Longitudinal ac field.

lowered further, more inclusions appear, the average conductivity increases still further, and eddy-current shielding becomes significant. χ'' then increases less rapidly, reaches a maximum, and finally starts to decrease as the shielding begins to dominate.

In order for the suggested average conductivity mechanism to be valid, the superconducting inclusions must be filamentary or in the form of thin flakes so as to increase the average conductivity and at the same time permit the magnetic field to penetrate as in a normal metal. This would not be the case if the inclusions occupied much volume and were, say spheroidal, or in the form of cylindrical regions, parallel to the axis of the rod. In that case, the decrease in resistance for the circumferential eddy currents would not increase the average dissipation, because the effective fraction of normal metal would be reduced proportionately. If the inclusions are randomly disposed thin filaments or flakes, occupying negligible volume, the only shielding effect is due to the eddy currents which are determined by the average conductivity of the structure until the point is reached where the filaments begin to form a multiply connected network or Mendelssohn sponge. The matrix may or may not become superconducting within the transition interval of the filamentary structure. In the example of Fig. 2(b), the matrix probably did become superconducting before completion of the transition in the filamentary structure. This would explain the weak maximum in χ''. However, in another sample, a cold-worked alloy of tin containing 0.87 % lead in solution, a large maximum in χ'' was observed, and the fact that the matrix became superconducting at a substantially lower temperature was verified by other data. In this alloy, the *filamentary transition*, as observed at a frequency of 18.2 cps, occurred at 3.89°K. A *dc ballistic susceptibility* measurement indicated a transition at 3.80°K, while the transition temperature of the *matrix*, as determined from specific heat measurements for another sample of the same alloy by Shiffman *et al.*,[4] was 3.72°K. The ac susceptibility measurement responds to the average conductivity mechanism described above and therefore detects the *early stages* in the development of a filamentary mechanism. The dc ballistic measurement detects the formation of closed loops in the filamentary structure, and its transition begins only when the ac transition is almost complete. Finally, the specific-heat measurement does not respond to the filamentary structure at all, but sees only the *bulk* material.

We have also observed the dependence of χ' and χ'' in these transitions on the amplitude of the exciting field and on the frequency. It is not feasible to describe these results in detail here, but the data are consistent with the average-conductivity filamentary model. We find that for ac measuring fields of the order of 0.004 oersted, the position of the peak changes more rapidly than 1 deg/Oe, which appears to be a critical current effect in the filaments.[5]

The results obtained thus far help to elucidate the nature of the filamentary structures. The sample of Fig. 2(a) exhibits a broad transition for a pure material, a result no doubt of the cold work in the extrusion process. The wire was extruded at room temperature and remained at room temperature for about 18 hours before being cooled to liquid helium temperatures. Although the transition is broad, probably due to the wide variation in the degree of distortion of the lattice near the dislocations, there is, however, no suggestion of a filamentary structure. The sample of Fig. 2(b) is also relatively pure, although only "three 9's" compared to the "five 9's" of Fig. 2(a). The degree of cold working was hardly more severe, yet this sample shows definite evidence of filamentary structure. It seems, therefore, that dislocations alone do not cause filamentary structure, but that some impurity content, if only nominal, is required in addition.[6] It has been recognized for some time that impurities tend to segregate out along dislocation lines, and this seems to be the mechanism operating in the samples we have studied. In the "three 9's" tin, the principal metallic impurity given in the batch analysis was 30 ppm of lead. If we were to visualize the lead atoms as migrating to the dislocations and forming chains with 3×10^{-8} cm between neighbors, there would be enough atoms per cc to clothe 10^{10} cm of dislocation line! While this picture is overly naive, it is clear than even a nominal lead impurity is enough to form a substantial number of filamentary inclusions when coupled with dislocations.

The cold-worked tin alloys, having the order of a percent of lead in solution, showed very large maxima. A one-percent alloy of this composition, which was not strained but consisted of a few large crystals, showed a smaller maximum comparable in size with that of Fig. 2(b). A "three 9's" niobium single crystal exhibited a small maximum in χ'', but a tantalum single crystal of slightly higher purity did not.

More extensive measurements on these and other materials are in progress. We believe, however, that some tentative deductions may be derived from the data thus far:

(1) The imaginary component of the complex susceptibility is a sensitive index of physical filamentary structure.

(2) Dislocations coupled with even small impurity content tend to form filamentary networks.

(3) Superconductors even when not intentionally strained may contain enough residual dislocations, so that when large impurity concentrations are present (of the order of a percent) detectable filamentary structure may occur.

Finally, we note that superconductors with physical filamentary networks of the kind described here would no doubt exhibit negative surface energy. The impurity content necessary to produce filaments would also decrease the mean free path and coherence distance, which conditions are favorable for the appearance of negative surface energy. In addition, the existence of impurity-clothed dislocations would offer many nucleation centers. However, we would not expect these superconductors to exhibit completely reversible transitions in a magnetic field, as the filamentary structures would trap flux. This type of structure may account for some of the irreversible transitions reported where negative surface energy phenomena have been noted.

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[1] L. D. Landau and E. M. Lifshitz, Electrodynamics of Continuous Media (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1960), p. 194. H. E. Rohrschach and M. A. Herlin, Massachusetts Institute of Technology Research Laboratory of Electronics Technical Report No. 125 (unpublished). N. W. MacLachlan, Bessel Functions for Engineers (Clarendon Press, Oxford, England, 1955), 2nd ed., p. 165.

[2] In principle, we should expect a maximum in χ'' for a homogeneous superconductor very close to the transition temperature when the penetration depth is comparable to the cylinder diameter. This would follow if we were to substitute for k in Eq. (1) an expression appropriate to a superconductor. In a London two-fluid model, for example,

$$k=(-2i/\delta^2-1/\lambda^2)^{1/2},$$

where δ and λ are both temperature dependent. This maxima, however, should occur so close to T_c that we would be unable to observe it in these measurements.

[3] There is a formal analogy between this process and a polarizable dielectric. The analogous dielectric problem would be the effect of increasing the average apparent dielectric constant of a medium by loading it with metallic particles insulated from one another.

[4] C. A. Shiffman, M. Garber, J. F. Cochran, E. Maxwell, and G. W. Pearsall, Bull. Am. Phys. Soc. 8, 66 (1963).

[5] The most striking feature of the frequency dependence is that the apparent transition (inflection point in χ' and

maximum in χ'') is shifted to higher temperatures with increased frequency.

[6] The influence of impurity-clothed dislocations has been discussed by R. W. Shaw and D. E. Mapother, Phys. Rev. 118, 1474 (1960), in connection with filamentary structure observed in magnetic transitions. Dislocations as a possible source of filamentary structure have also been discussed by others, e.g., J. E. Kunzler, Rev. Modern Phys. 33, 501 (1961); J. J. Hauser and E. Buehler, Phys. Rev. 125, 142 (1961).

DOUBLE ACCEPTOR DEFECT IN CdTe†

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In the course of studying the electrical properties of high-purity single crystals of CdTe, a new center, thought to be a native double acceptor, has been observed. It is believed to be the first of its kind in compound semiconductors identified by electrical transport measurements. This center is formed during heat treatment in a Cd atmosphere. The doubly ionized acceptor level lies 0.056 eV below the conduction band, and when this level is filled the center contains two electrons and is an effective hole trap at low temperatures. In fact, the singly negatively charged center has such a low cross section for electron capture that it is impossible to observe a normal freeze-out of electrons into the second level when the samples are cooled below a critical temperature region. A similar level about 0.09 eV below the conduction band has also been found in CdS.

CdTe samples were prepared by techniques already described.[1] High-purity crystals having a residual impurity donor concentration of about 10^{15} cm^{-3} were used.[2] Hall bars of approximately $3 \times 3 \times 10$ mm^3 were sealed in small evacuated quartz ampoules to which Cd metal was added. These were heated to various temperatures for varying lengths of time and then quenched. The surface regions of the samples were removed by grinding, etching, and a final chemical polish. The crystals were then studied using conventional dc techniques to measure the Hall coefficient, resistivity, and Hall mobility from 350°K to 12°K. There were provisions for exciting the samples with a small incandescent lamp mounted inside the cryostat.

The temperature dependence of the Hall constant for electrons in several samples is shown in Fig. 1. Curve *A* represents an unfired sample; curve *B*, a sample fired at 900°C for 30 min; and curve *C*, a sample fired at 900°C for 285 h. The solid curves correspond to measurements without light, and the dashed curves show the effects following photoexcitation at the lowest temperature. Freeze-out of electrons into the level of interest starts near 300°K and is most pronounced in curve *B*. The thermal activation energy is 0.056 eV. At about 110°K the electronic equilibrium

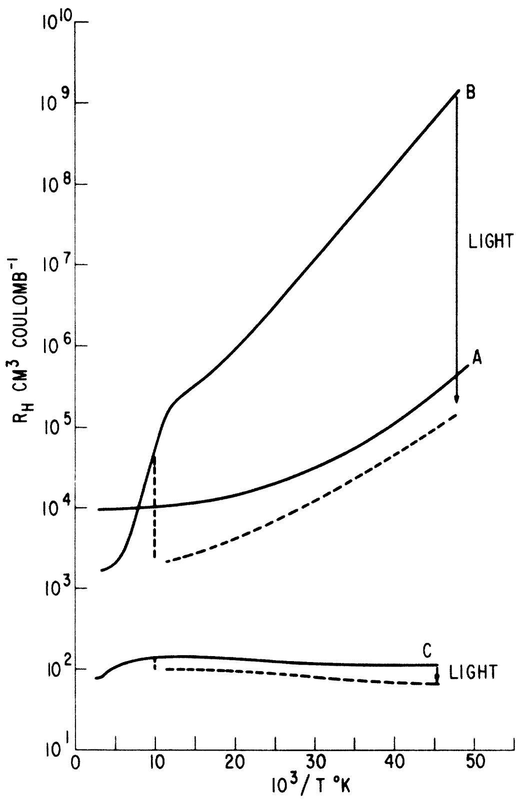

FIG. 1. The temperature dependence of the Hall coefficient, R_H, of *n*-type CdTe samples. The dashed curves show R_H after photoexcitation at the lowest temperature. *A*: original high-purity material; *B*: Cd fired for one-half hour at 900°C; *C*: Cd fired for 285 hours at 900°C.