

resonance of  $\text{Cr}^{53}$  by the onset of magnetic ordering provides a convenient and sensitive means of delineating the dependence of  $T_N$  upon alloy composition, and hence upon electron concentration.

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## MAGNETIZATION OF HARD SUPERCONDUCTORS

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It has long been recognized that the magnetic properties of hard superconductors differ qualitatively from those of soft superconductors. Specifically, the hard superconductors often exhibit hysteresis and, in addition, display superconducting properties in fields that are far greater than the critical fields of soft superconductors. In addition it is becoming increasingly clear that these two types of material differ in their microstructure. Confirming Mendelssohn's postulate,<sup>1</sup> the hard superconductors possess, in many cases, a filamentary mesh structure in which the diameter of the filaments is less than the London penetration depth. Shaw and Mapother<sup>2</sup> have recently given a discussion of Mendelssohn's hypothesis and propose a special filamentary arrangement to explain qualitatively the hysteresis they observed in the magnetic transition of plastically deformed lead.

To derive the magnetic properties of such a structure, we could start from first principles. I shall, however, treat the problem macroscopically. I shall assume the filamentary structure to be capable of sustaining lossless macroscopic current up to a critical current density,  $J_C$ . This critical current density is a function of magnetic field. It becomes zero at the critical field of the filaments. In the treatment that follows I assume that the critical current density is independent of field which is equivalent to the assumption that the applied fields are much less than the critical

fields of the filaments. I also assume that the interstices of the mesh are fitted with a soft superconductor of critical field  $H_C$ . Lastly I assume that the magnetic field is shielded by the soft superconductor to a field  $H_C$ ; then further shielding is accomplished by currents flowing in the filamentary mesh. These currents flow to the full amount  $J_C$  for a depth necessary to reduce the field to  $H_C$ .

To derive the magnetization curve of a virgin hard superconductor we must calculate the internal field  $H_i$  as a function of position in the superconductor and as a function of the external field. By definition, the magnetization  $M$  is given by

$$4\pi M = \int (H_i - H) dv / \int dv, \quad (1)$$

where the integrals are over the volume of the specimen. In order to compare the results of this theory with experiment, I shall assume the field to be applied parallel to the axis of a circular cylinder of radius  $R$ . If the applied field is less than  $H_C$ , the shielding is complete if  $R$  is much greater than the London penetration depth. This gives

$$H_i = 0; \quad 0 \leq r \leq R, \quad 0 \leq H \leq H_C. \quad (2)$$

As the field is further increased, the soft superconductor on the outside becomes normal and

currents are induced to flow in the filaments. If the field is an amount  $H-H_c$  above the bulk critical field, then by the circuital form of Ampere's law, filamentary currents must be flowing to a depth  $\Delta$  from the surface, where  $\Delta=10(H-H_c)/$

$4\pi J_c$ . This new macroscopic, field-dependent penetration depth is the core of this theory. If we designate a new field,  $H^* = 4\pi J_c R/10$ ,<sup>3</sup> then we have the following internal fields in the next stage of magnetization:

$$\left. \begin{aligned} H_i &= 0; & 0 \leq r \leq R[1 - (H - H_c)/H^*], \\ H_i &= H - H^*(1 - r/R); & R[1 - (H - H_c)/H^*] \leq r \leq R, \end{aligned} \right\} H_c \leq H \leq H^* + H_c. \tag{3}$$

Lastly when all the bulk properties have been destroyed, only the filamentary currents flow and we have

$$H_i = H - H^*(1 - r/R); \quad 0 \leq r \leq R, \quad H^* + H_c \leq H. \tag{4}$$

Putting Eqs. (2), (3), and (4) into Eq. (1) and integrating, we obtain the magnetization as

$$4\pi M = -H; \quad 0 \leq H \leq H_c$$

$$4\pi M = -H + (H^2 - H_c^2)/H^* + [H_c^2(3H - 2H_c) - H^3]/3H^{*2};$$

$$H_c \leq H \leq H^* + H_c$$

$$4\pi M = -H^*/3; \quad H^* + H_c \leq H.$$

Figure 1 shows the initial magnetization curves predicted by this theory plotted in dimensionless units. The plot,  $H^* = 0$ , illustrates the behavior of the pure, soft superconductor while the other curves show the behavior expected for various values of  $H^*$ . By the definition of  $H^*$ , these correspond to various products of radius and critical current density.

The striking result of this theory is that the magnetization of a filamentary superconductor is expected to depend on the macroscopic dimensions of the sample. To check this aspect of the theory we have measured the initial magnetization of a cylinder of Nb<sub>3</sub>Sn ground successively to two radii. The sample, prepared under the super-

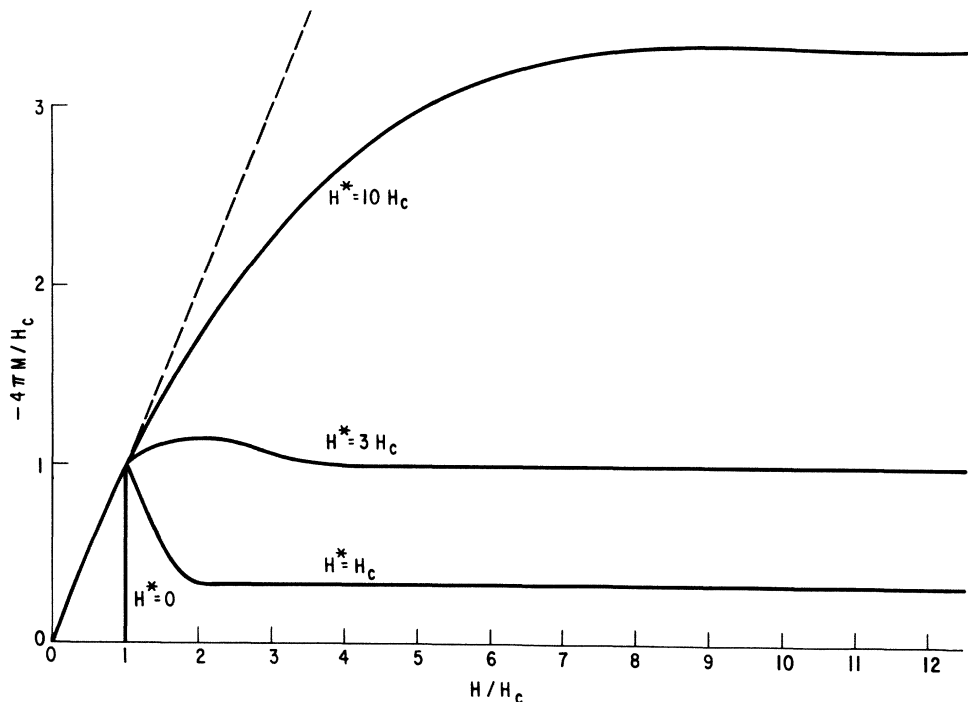


FIG. 1. Magnetization as a function of field for a cylindrical filamentary superconductor. In this plot,  $H_c$  is the critical field in the interstices of the filaments, while  $H^* = 4\pi J_c R/10$  is a measure of the critical current density  $J_c$  (assumed independent of field) and the radius  $R$  of the cylinder.

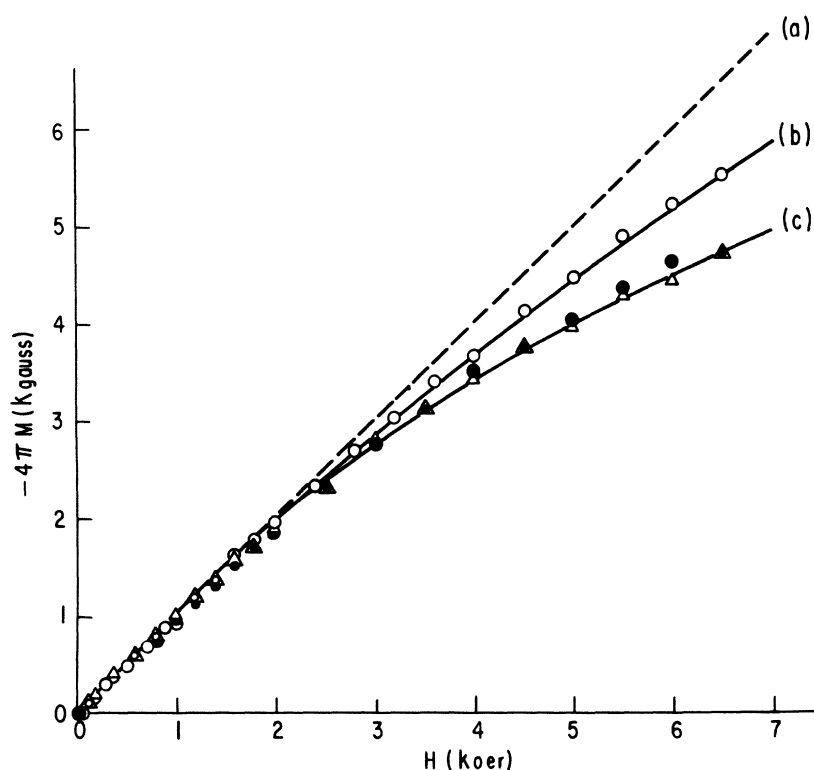


FIG. 2. The magnetization curves of  $\text{Nb}_3\text{Sn}$  samples of two diameters, at  $4.2^\circ\text{K}$ . The dashed line, (a), shows the magnetization expected for a perfect diamagnet. The open circles, o, show the experimental results on a sample of 0.48 cm diameter, while the closed circles, ●, and open triangles,  $\Delta$ , represent two samples of 0.25 diameter. The solid curves, (b) and (c), are theoretical curves calculated on the assumption that the bulk critical field is 2000 oe and the material will carry a lossless current density of  $1.2 \times 10^5$  amperes/cm<sup>2</sup>.

vision of A. Seybolt, was formed from a hydrostatically pressed powder mixture that was vacuum sintered at  $1200^\circ\text{C}$  for 8 hours. A cylinder, 0.48 cm in diameter and 1.9 cm long, was ground out of the sintered mass. Its magnetization curve is shown as the open circles in Fig. 2. The specimen was then ground down to 0.25 cm. It broke in two almost equal parts and both were measured as indicated by the closed circles and open triangles in Fig. 2.

The solid lines are theoretical curves based upon the assumption of a bulk critical field in the interstices of 2000 oe and in addition that the material will support a current density of  $1.2 \times 10^5$  amp/cm<sup>2</sup>. It is tempting to identify the critical field with that of impure niobium. Pure bulk niobium has a critical field of about 1600 oe at this temperature.<sup>4</sup>

An alternate explanation of high-field superconductivity has been offered in detail by Abrikosov<sup>5</sup> and later by Goodman<sup>6</sup> who invoke the concept of negative surface energy in a superconductor of short mean free path. They point out that under these conditions, the superconductor will spontaneously break up into filaments and they derive curves very similar to those of Fig. 1. There is a striking difference between this theory

and the filamentary theory treated above. With the negative surface energy theory there is no thickness dependence in a long solid as there is with the filamentary model. This difference will be useful in assigning various experimental situations to one or the other of these pictures.

Another difference between the theories noted above and that developed in this communication lies in the assumption in the former cases of complete thermodynamic equilibrium. Hence they predict no hysteresis in the magnetic properties while such hysteresis, e.g., trapped flux, follows from the filamentary model and may be exactly calculated. In this connection, it is appropriate to recall that Pippard originally proposed<sup>7</sup> that superconductors of short mean path should be hysteretic.

I wish to thank Mrs. Margaret V. Doyle for aiding in the experimental observations. A. U. Seybolt supervised the preparation of the specimen. In addition, I have profited from discussions with J. C. Fisher and P. S. Swartz.

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<sup>3</sup>While  $H^*$  is used mainly to simplify the analytical expressions, physically it is the field that must be applied to the specimen in excess of the bulk critical field in order that critical currents may be induced to flow through the entire specimen. In other words, the penetration depth  $\Delta$  is equal to the radius  $R$  when this condition obtains.

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## INFRARED RESONANCE FLUORESCENCE IN THE FUNDAMENTAL VIBRATION-ROTATION BAND OF CARBON MONOXIDE\*

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The collisional deactivation of vibrationally excited diatomic molecules is known to be a slow process at low temperatures. Indeed, for carbon monoxide gas at 300°K and one atmosphere pressure, a time constant of five seconds is indicated by extrapolating the vibrational relaxation data of Matthews<sup>1</sup> and of Hooker.<sup>2</sup> A long extrapolation is required, however, since those shock tube data cover the 4900-1100°K range. In contrast, the radiative lifetime of vibrationally excited CO deduced from absorption measurements is 0.03 second.<sup>3,4</sup> If the extrapolation is valid, then at room temperature the loss of vibrational excitation by radiation should be 160 times faster than loss by collision. This suggested that an infrared fluorescence experiment would be possible if the deactivating effect of impurities and wall collisions could be avoided. This note reports the results of such an experiment.

We have observed fluorescence of carbon monoxide gas (300°K, 1 atm) in its fundamental vibration-rotation band centered at 2143  $\text{cm}^{-1}$ . The problem of wall collisions was eliminated by using an "open-air" flow system in which the CO sample was contained in a surrounding flow of argon. We have found that CO-Ar collisions are less effective in deactivating vibrationally excited CO molecules than are CO-CO collisions.

Carbon monoxide (Matheson, cp grade), obtained from a tank through pressure regulators and a critical orifice flowmeter, was passed through two cold traps, one at -80°C and one at -150°C, for purification. The gas issued from a 3.5-cm diam porous disk with a laminar flow velocity of 10 cm/sec. This flow of CO was surrounded by a 1.2-cm wide annular argon flow of matched veloc-

ity. The composite stream was illuminated 2 cm above the gas ports from two opposing sides with collimated light from 2500°K zirconia sources. The infrared fluorescence was observed in the same plane, but at right angles to the beams of exciting light with an infrared spectrometer set to accept the entire 1900 to 2300  $\text{cm}^{-1}$  region. The response of the spectrometer was calibrated by keeping the exciting lights off and thermally heating the gas flow with hot water coils imbedded in the porous disks. A gas temperature rise of 2°C was detectable with a signal-to-noise ratio of unity. When the exciting lights were turned on, a signal was observed equivalent to a 30°C gas temperature rise. Convincing evidence that the exciting lights were heating the gas 30°C in a nonequilibrium fashion was obtained by warming the second cold trap in the CO line from -150°C to -120°C. This permitted one percent of CO<sub>2</sub> to enter the gas stream. The signal vanished. Recooling the trap to -150°C restored the signal. This quenching of the signal by impurities shows that we are observing fluorescence, for equilibrium emission from the CO, or even scattered light, would not be so affected.

The radiative lifetime of the first excited vibrational state of CO has been determined by exciting the flowing CO stream at one position, and measuring the decay of the fluorescence at several points downstream. For known flow velocities the elapsed time between excitation and detection is easily calculated. For pure CO we found that the decay of the fluorescence was nearly exponential, but the deduced time constant was over four times the value given by absorption intensity measurements.<sup>3,4</sup> Suspecting that the