hibit absorption bands far closer to the laser frequency. We have performed some initial experiments with CdS which are inconclusive at the present time due to the large pyroelectric and photoconductive effects in this material.

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³P. A. Franken and J. F. Ward (to be published).

 $^{4}\mathrm{Trion}$ Instruments Model No. LS-2 with MH1 OPTUL attachment.

EVIDENCE FOR THE NEGATIVE SURFACE ENERGY MODELS OF SUPERCONDUCTIVITY IN Nb₃Sn, Nb₃Al, V₃Ga, AND V₃Si

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Large specimens (diameter greater than about 1 mm) of natural high-field superconductors,^{1,2} such as Nb₃Sn, and synthetic high-field superconductors³ (interconnected 30Å mercury filaments imbedded in Vycor glass) exhibit nearly identical magnetization loops. These loops, shown in somewhat idealized form in Fig. 1, have the following distinguishing features:

(1) The applied magnetic field H_a penetrates to the center of the specimen when it reaches the magnitude $4\pi J_I R/10$, where J_I is the superconducting current density in A/cm^2 induced to flow within the bulk of the specimen by the applied magnetic field, and R is the radius (cm) of the cylindrical specimen. In Fig. 1, J_I is assumed to be a constant independent of magnetic field up to the critical field.

(2) For applied magnetic fields $>4\pi J_I R/10$, but

less than the critical field, the magnetization is given by

$$-4\pi M = 4\pi J_{I} R/30.$$
 (1)

(3) The magnetization loop is symmetric about the horizontal axis.

It is interesting to note parenthetically that these features imply the existence of concentric superconducting current-carrying loops which are activated by the applied magnetic field.

If high-field superconductivity in the natural high-field superconductor originates solely from the presence of physically real superconducting filaments, as is the case for the synthetic highfield superconductor, then the magnetization loops of the natural high-field superconductor must close symmetrically about the horizontal axis with decreasing specimen size in accordance with



FIG. 1. Magnetization loop of large cylindrical specimens of both natural and synthetic high-field superconductors. J_I is the superconducting current density in A/cm² induced to flow within the bulk of the specimen by the applied magnetic field, and R is the radius (cm).



FIG. 2. Experimental magnetization loops of Nb₃Sn and V₃Ga for various particle sizes. The magnetization loops are converging to a negative surface energy magnetization curve (hatched curve). The magnetization curves of the $10-20\mu$ and $1-2\mu$ particles are not initially perfectly diamagnetic because of London penetration effects.

Eq. (1).

I have found, however, that the magnetization loops of powdered Nb₃Sn, Nb₃Al, V₃Ga, and V₃Si do not close symmetrically about the horizontal axis with decreasing particle size⁴ (Fig. 2). The $60-75\mu$ and $30-45\mu$ particles appear to be converging to a magnetization loop lying completely above the horizontal axis for applied fields of one sign and completely below for applied fields of the opposite sign. The powders in the $10-20\mu$ range and less exhibit asymmetric magnetization loops which are not initially perfectly diamagnetic. The magnetization of the $1-2\mu$ Nb₃Sn powder shown in Fig. 2 has the features that (1) it is initially only VOLUME 9, NUMBER 11

about 25% diamagnetic, (2) its maximum magnetization occurs at a higher applied field than the larger powders, and (3) its magnetization in applied fields greater than ~4000 Oe lies along the curve to which the heavier particles seem to be converging.

The experimental magnetization curves are consistent with the following interpretations. The magnetization loop of intermetallic high-field superconductors is the sum of two loops, one which is size independent until London penetration effects⁵ become inportant and lies above the horizontal axis for applied magnetic fields of one sign and below for the opposite sign, and a second which is size and current-density dependent and symmetric about the asymmetric loop. This asymmetric magnetization loop (hatched curve in Fig. 2) is perfectly diamagnetic only to a few hundred oersteds.

The asymmetric magnetization loop has a form very similar to that predicted by the negative surface energy models of superconductivity.⁶⁻⁸ According to these models a superconductor will, under certain circumstances, exhibit perfect diamagnetic behavior only to some magnetic field H_{fb} rather than to its thermodynamic critical field H_c . At H_{fb} the flux penetrates and the superconductor enters a mixed state characterized by the formation of normal filamentary regions, each housing one fluxoid. The superconductor returns completely to the normal state at some magnetic field H_n greater than the thermodynamic critical field. Magnetization curves of the form shown in Fig. 3 are expected. From thermodynamic arguments the area under this curve is $\frac{1}{2}H_c^2$.

The superconductor V_3 Ga has a thermodynamic critical field H_c of 6 kOe.⁹ The results presented

in Fig. 2 indicate that V_3 Ga remains perfectly diamagnetic only to about 400 Oe. If this value is identified with H_{fp} , then H_n is calculated to be about 350 kOe^{8,10} at 4.2°K, in agreement with the extrapolated value.⁹

The characteristic sharp change in the magnetization expected at H_{fp} does not appear with the powders, presumably because of the nonzero demagnetizing factor of each particle, the spread of particle sizes and shapes, and the effects of the remaining size-dependent hysteresis.

The magnetization of the $1-2\mu$ powder is also consistent with the negative surface energy model. Initially the powders are not perfectly diamagnetic because of London penetration effects.⁵ Consequently the fluxoids do not enter until some magnetic field greater than H_{fp} observed in the larger specimens. Hence the magnetization goes through a maximum at higher applied field. At high magnetic fields (>4000 Oe) the number of fluxoids in each particle is large and the magnitude of the magnetization falls along the hatched curve.

The identification of the asymmetric magnetization loop as an intrinsic bulk property gains support from the following additional evidence. I have found that the extrapolated asymmetric magnetization loop is the same both for varied methods of production (arc casting, diffusion process, and induction melting) of the parent Nb₃Sn ingot and for varying oxygen content. The magnetization curves differed only in the magnitude of the sizedependent loop. The diffusion Nb₃Sn exhibited an order of magnitude more size-dependent magnetization than the same size particle crushed from induction-melted or arc-cast Nb₃Sn.

The size-dependent contribution to the total magnetization loop in large specimens which obscures



FIG. 3. Form of the negative surface energy magnetization curve. H_{fp} is the field at which the fluxoids penetrate; H_c is the thermodynamic critical field; H_n is the field which completely destroys superconductivity.

Table I. Summary of results in terms of J_I , the induced superconducting current density, and H_{fp} , the magnetic field at which fluxoids first penetrate into the superconductor.

Material	H _{fp} (Oe)	J_I at H_a = 2000 Oe (A/cm ²)
Diffusion process Nb 3 Sn	400 ± 100	10×10^{4}
Arc-cast Nb ₃ Sn	350 ± 75	1×10^4
Arc-cast Nb ₃ Al	375 ± 75	2×10^4
Arc-cast V ₃ Ga	400 ± 100	$8 imes 10^4$
Arc-cast V ₃ Si	550 ± 75	2×10^{4}

the intrinsic magnetization could originate from loops of extended flaws,¹¹ if these flaws interact with the fluxoids in such a way as to support a change in the density of fluxoids. Such a density gradient is equivalent to the postulated loop currents.

The powder specimens measured were obtained from a parent ingot by crushing, sizing, and then blending (to about 40 volume %) with Fisher Nonac stopcock grease which electrically insulated the particles from one another. The slurry was packed into a paper straw or glass tube $(\sim \frac{1}{8}$ in. diameter, $\sim \frac{1}{2}$ in. long) and cooled to 4.2°K. The magnetic measurements were made by the method described in reference 3.

Table I summarizes the results for the four intermetallics in terms of two parameters H_{fp} and J_I .

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OSCILLATORY QUANTUM EFFECTS IN THE ULTRASONIC VELOCITY IN BISMUTH

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We have observed oscillatory changes in the velocity of sound in bismuth at 4° K as a function of magnetic field. The classical quadratic variation of the velocity of sound with magnetic field has been previously observed¹ in the metals Sn, Al, and Mg at room temperature. It has been suggested² that quantum effects, analogous to the de Haas – van Alphen effect, in the velocity of sound should also occur. The conditions for the observation of quantum effects in the sound dis-

persion are the same as those required to observe such effects in other transport phenomena, i.e., the magnetoresistance and thermal conductivity. These conditions are (1) that $\hbar\omega_c > kT$ and (2) that $\omega_c \tau > 1$, where ω_c is the cyclotron frequency (= eH/m^*c). Physically these conditions are required so that the broadening of the Landau levels due to electron scattering, either because of thermal vibrations or impurities, will not be great enough to smear out the oscillations.