Anisotropic Meissner Effect in the Linear-Chain Mercury Compound $Hg_{2.86}AsF_6$

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Magnetization measurements on single crystals and powders of $Hg_{2.86}AsF_6$ show flux expulsion when samples are cooled in a small magnetic field, indicating superconductivity below 4.1 K. The observation of anisotropic flux expulsion with magnitude dependent upon the orientation of the external field with respect to the crystalline axes confirms the anisotropic superconductivity first observed in conductivity measurements.

We report in this Letter the results of a study of the Meissner effect in the incommensurate linear-chain metal $Hg_{2.86}AsF_6$.[1-6] The results of magnetization (M) measurements at low temperatures ($1.2\ \mathrm{K} < T < 4.2\ \mathrm{K}$) and low magnetic fields ($0.015\ \mathrm{G} < H < 100\ \mathrm{G}$) indicate that this compound is an anisotropic superconductor. The magnetization results differ from the usual Meissner effect in three respects. First, the flux expulsion is anisotropic; i.e., the magnitude depends strongly on the orientation of the applied field with respect to the crystalline axes. Second, the temperature dependence of the flux exclusion is not a step function, but rather a continuously increasing function for $T < T_c$. Third, $4\pi M/H$ is field dependent even at fields less than 10^{-4} of the thermodynamic bulk critical field.

The crystal structure[2,7] of $Hg_{3-\delta}AsF_6$ ($\delta = 0.18$ at room temperature)[8] consists of a host tetragonal array of AsF_6 octahedra and nonintersecting linear mercury chains running parallel to the $\vec{a}$ and $\vec{b}$ axes.[2,7] There are no chains along the $\vec{c}$ direction. The intrachain Hg-Hg distance is 2.66 Å.[8] Since the unit-cell parameters are $a = b = 7.55$ Å, the mercury chains are incommensurate with the three-dimensional host lattice. The shortest distance between the chains along the $\vec{c}$ axis is 3.09 Å, and is comparable to the interatomic distance in mercury metal.

In our previous studies,[4] measurements of the electrical resistivity of $Hg_{2.86}AsF_6$ were carried out with use of generalized Montgomery and contactless ac eddy-current techniques. The room-temperature resistivity, ρ_{ab}, along the chain directions was found to be $10^{-4}\ \Omega$ cm with anisotropy $\rho_c/\rho_{ab} \sim 10^2$ and a temperature dependence consistent with a simple power law, $\rho_{ab} \sim T^n$ where $n \simeq 1.5$. Low-temperature measurements showed no indication of residual resistance at temperatures as low as 1.4 K with a measured resistance ratio $\rho_{ab}(300\ \mathrm{K})/\rho_{ab}(1.4\ \mathrm{K}) \simeq 3000$. Near 4 K, we found that the c-axis resistivity dropped abruptly by more than three orders of magnitude, apparently to zero, while ρ_{ab} was continuous. The c-axis transition was suppressed in a small magnetic field, implying the onset of superconductivity. However, since resistivity measurements cannot distinguish bulk superconductivity from a filamentary effect, the fundamental origin of the the c-axis superconductivity remained open, particularly since the observed transition ($T_c = 4.10$) is close to that of free Hg (4.15 K).

The Meissner effect was observed on single-crystal samples and on powders. In each case, the sample was cooled in a constant external field, and the induced magnetic moment was measured with a superconducting quantum interference device (SQUID) magnetometer. The magnetic fields ($0.015\ \mathrm{G} < H < 100\ \mathrm{G}$) were calibrated with a single crystal of MnF_2 and are accurate to $\pm 1\%$. Temperatures ($1.6\ \mathrm{K} < T < 4.2\ \mathrm{K}$) were measured using a diode which was calibrated at several fixed points with superconductors (T_c) and between the fixed points with neodymium ethyl sulfate. Different orientations of the crystals with respect to the vertical applied field were obtained by inserting samples cut and oriented in sealed glass tubes with $\vec{a}$ axis, $\vec{a}+\vec{b}$ axis, or $\vec{c}$ axis vertical. The powder data were supplemented by low-frequency ac measurements using a mutual-inductance bridge in the range $1.2\ \mathrm{K} < T < 4.2\ \mathrm{K}$.

The crystals were grown[1,9,10] from a mercury

surface in contact with a solution of arsenic pentafluoride (AsF_5) in liquid SO_2 at room temperature. Although the elemental analysis indicates a composition close to Hg_3AsF_6, neutron diffraction studies[7,8] of single crystals verified the x-ray results obtained for $Hg_{3-\delta}AsF_6$ by Brown *et al.*[2] Samples were sealed in 3-mm-i.d. glass tubes, with the crystal axis along which the field was to be applied oriented along the tube (vertical) axis. In order that all samples had roughly the same shape (cylindrical) and occupied roughly the same volume (~0.03 cm^3), each sample consisted of two or three oriented pieces stacked in contact. Powder samples were of similar volume.

The resulting data for $-4\pi M/H$ are shown in Fig. 1 for an applied magnetic field of $H_0 = 0.015$ G. When the external field is applied in the crystallographic a-b plane, a large temperature-dependent diamagnetism is observed indicative of 20% flux expulsion at 1.6 K in 0.015 G. Even at $T/T_c < 0.5$, the magnitude is increasing toward larger values. For $\vec{H} \| \vec{c}$, the onset of flux expulsion occurs at precisely the same temperature. However, as shown in Fig. 1, the measured magnetic moment is more than an order of magnitude (approximately a factor of 15) smaller with $\vec{H} \| \vec{c}$ than with $\vec{H} \| \vec{a}$.

A smaller anisotropy is observed in the a-b plane. Measurements with $H = 0.015$ G applied along a (110) direction, $\vec{H} \| (\vec{a} + \vec{b})$, gave results approximately 25% larger than for $\vec{H} \| \vec{a}$. Demagnetization corrections estimated from the sample shapes and measured magnetization are less than about 5%.

In addition to single-crystal studies, we have carried out measurements on fine- and coarse-powdered samples. We find that in all cases the data from powdered samples are consistent with a simple powder average, $M(\text{powder}) \simeq \frac{1}{3} M(\vec{H} \| \vec{c}) + \frac{2}{3} M(\vec{H} \| \vec{a})$, to within an accuracy limited by the small anisotropy observed in the a-b plane. The powder data for $H = 0.015$ are shown in Fig. 1.

A comparison of the dc flux expulsion and the ac susceptibility is also shown in Fig. 1. Because of the high a-b plane conductivity, low-frequency ac measurements on single crystals inevitably lead to eddy-current effects, whereas the powder data avoid such difficulties. The ac and dc results are in agreement. The ac data extend the temperature range down to 1.2 K and show a clear indication of an upturn toward complete flux explusion at the lowest temperatures.

The experimental results for $-4\pi M/H$ exhibit an unusual magnetic-field dependence. The data for $\vec{H} \| (\vec{a} + \vec{b})$ are shown in Fig. 2 for applied magnetic fields of $H = 0.015$, 0.12, 1.0, 10, and 100 G. Figure 2 demonstrates that the magnitude of the incomplete Meissner effect is a function of field even at $H/H_c < 4 \times 10^{-5}$, where $H_c = 380$ G is the critical field obtained from resistance meas-

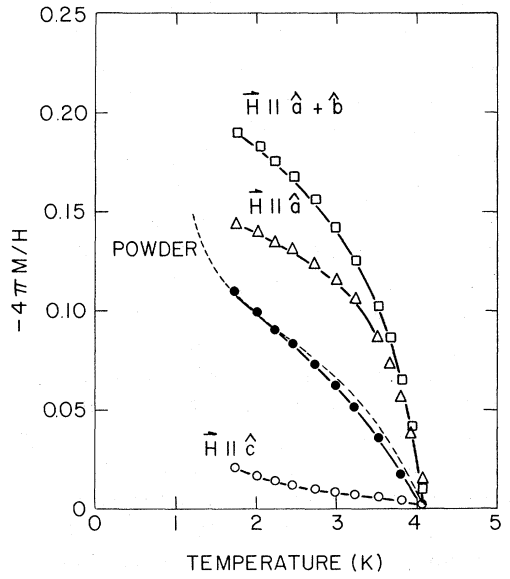

FIG. 1. Temperature dependence of $-4\pi M/H$ at $H = 0.015$ G for single crystals and a powder sample. The dashed curve represents the ac-susceptibility ($\nu = 500$ Hz) data for the powder sample.

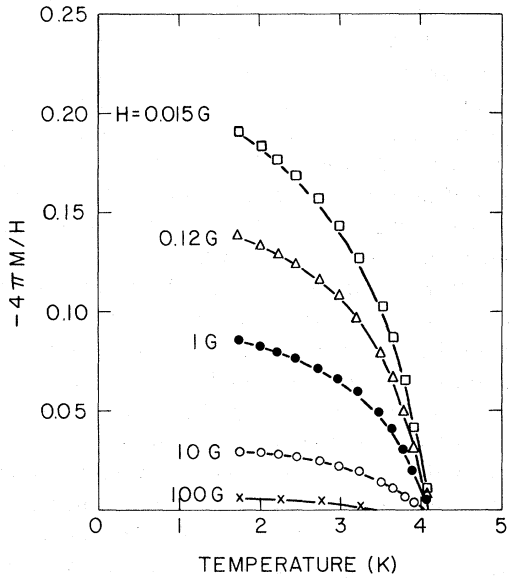

FIG. 2. Temperature dependence of $-4\pi M/H$ at different magnetic fields for a single-crystal sample; $\vec{H} \| (\hat{a} + \hat{b})$.

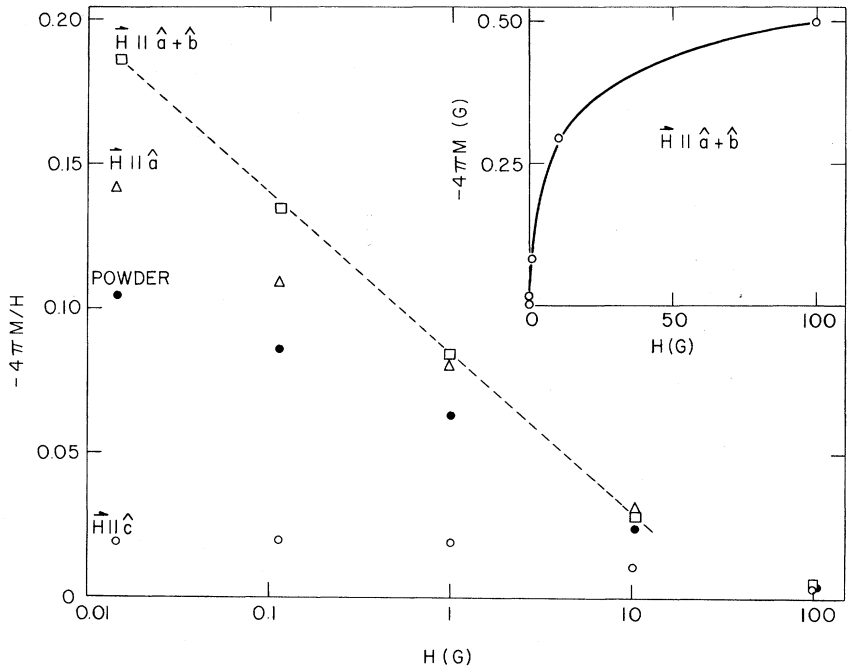

FIG. 3. Field dependence of $-4\pi M/H$ at 1.9 K. The inset shows the magnetization curve, $-4\pi M$ vs H.

urements at 1.4 K. The uniform increase in $-4\pi M/H$ with decreasing field makes extrapolation to zero field impossible, but complete flux expulsion is not ruled out by the data.

The lowest-temperature (1.9 K) results are replotted in Fig. 3 as $-4\pi M/H$ vs $\ln H$. The logarithmic behavior for $\vec{H} \| (\vec{a}+\vec{b})$ over more than three orders of magnitude in H as shown by the dashed line on Fig. 3 implies that empirically $-4\pi M/H = \chi_0 \ln(H/H_0)$, with $\chi_0 = -0.055$ and $H_0 = 35$ G. Also shown in Fig. 3 are the results for $\vec{H} \| \vec{c}$; in this case, $-4\pi M_c/H$ is independent of field.

The observation of flux expulsion with the magnitudes indicated in Figs. 1–3 provides additional evidence of superconductivity below 4 K, and implies that the superconductivity is intrinsic and does not arise from a small volume of interconnected free Hg filaments. The latter would be expected to trap flux rather than expel it. The agreement between the static flux exclusion and ac susceptibility indicated in Fig. 1 shows that there is no evidence of trapped flux due to multiply connected superconducting regions. Moreover, the large anisotropy and unusual temperature and field dependence appear to be inconsistent with filamentary effects. An array of superconducting Hg filaments weakly coupled by intervening metal might lead to bulk superconductivity through the proximity effect. However, such a system would be expected to show isotropic flux exclusion, particularly at low fields. Anistropy can arise from internal-field corrections due to the demagnetization field. However, in the extreme case of long cylinders, the maximum anisotropy would be 2:1 whereas the experimental values are an order of magnitude larger at low fields.

The strong field dependence of Figs. 2 and 3 is reminiscent of flux penetration in a type-II superconductor above H_{c1}. However, the observation from resistance measurements[4] of critical fields ($H_c \simeq 380$ G at 1.4 K) consistent in magnitude with $T_c \simeq 4$ K appears to rule out such an interpretation. Moreover, the results shown in Figs. 2 and 3 would imply $H_{c1} < 0.015$ G, or $H_c/H_{c1} = \sqrt{2}\,\kappa > 2 \times 10^4$ where H_c is the thermodynamic critical field and κ is the Ginsburg-Landau parameter. For a typical value for the penetration depth, $\lambda \simeq 500$ Å, such a low value for H_{c1} would require ($H_c/H_{c1} \simeq \gamma/\xi$) a coherence length $\xi < 10^{-2}$ Å. Finally, simple type-II effects will not explain the large anisotropy, the shape of the magnetization curves, or the continuity of σ_{ab} through the phase transition. However, a detailed discussion of the temperature dependence, field dependence, and anisotropy of the Meissner effect must await an understanding of the anisotropy, magnitude, and field dependence of the penetration depth in such an anisotropic superconductor.

The observation of a Meissner effect with σ_{ab} finite suggests the possibility of an extended fluc-

tuation regime. Although finite, σ_{ab} might have a substantial contribution from superconducting fluctuations in order to allow a finite Meissner effect. The analogy with the work of Golub *et al.*[11] on fluctuation diamagnetism above T_c is instructive. They envision regions of order of the coherence length fluctuating into the superconducting state and partially excluding flux. Similar effects may be playing a role in this mercury chain compound. The apparent absence of residual resistance in the a-b plane[4] down to 1.4 K and the unusual magnetic-field dependence of the resistivity with $\omega_c\tau \ll 1$ (Ref. 4) are consistent with this interesting possibility. Alternatively, taken at face value, the experimental results below 4 K can be viewed as evidence of anisotropic superconductivity. If this is indeed the case, the possibility of non-s-wave pairing in this anisotropic metal is worthy of speculation.

In summary, the discovery of a Meissner effect when samples of $Hg_{2.86}AsF_6$ are cooled in a small magnetic field provides evidence of bulk superconductivity below 4.1 K. The observation of anisotropic flux expulsion dependent upon the orientation of the external field with respect to the crystalline axes confirms the anisotropic superconductivity first observed in the transport measurements.

We are indebted to Dr. George Candela of the National Bureau of Standards for making available to us the use of a SQUID magnetometer, designed by Superconducting Technology, and for helping to identify and solve the special problems which arose due to the extremely low fields and pumped helium temperatures at which the experiments were carried out. We were impressed by the ease with which high-resolution data critical to the present study could be obtained under such conditions. This work was supported by the National Science Foundation Materials Research Laboratory Program under Grant No. DMR76-00678.

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[10]N. D. Miro, A. G. MacDiarmid, A. J. Heeger, A. F. Garito, C. K. Chiang, A. J. Schultz, and J. M. Williams, to be published. Under certain growth conditions, an adduct of composition $Hg_{2.86}AsF_6 \cdot y\,AsF_3$ $(0 < y < 1)$ is obtained. However, neutron diffraction studies show identical crystal structures with no sign of AsF_3, and electrical and optical properties indistinguishable from those of $Hg_{2.86}AsF_6$. Evidently the AsF_3 reaction product is physically entrained or occluded in such crystals during growth.

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