Pressure and temperature dependence of the superconducting state in $Hg_{3-\delta}AsF_6$

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The pressure (0—14 kbar) and the temperature (0.3—4.2 K) dependences of the magnetic susceptibility of the mercury chain crystal $Hg_{3-\delta}AsF_6$ are reported. We find that hydrostatic pressure suppresses both of the superconducting transition temperatures. The behavior of the upper transition temperature is discussed in terms of the elemental Hg inclusions inside the crystal which appear to nucleate the anisotropic superconductivity. The possibility of the existence of triplet superconductivity in $Hg_{3-\delta}AsF_6$ associated with the lower transition temperature is discussed as well.

I. INTRODUCTION

The unusual results of electrical transport, structure, and magnetic studies of the linear-chain conductor $Hg_{3-\delta}AsF_6$ have been of considerable interest.[1] Among all the fascinating phenomena which this crystal exhibits, the least understood are the anisotropic superconductivity[2,3] and the lack of a residual resistivity in the normal state.[2] In this paper we shall consider the effect of pressure on the superconducting state in this crystal.

The room-temperature resistivity ρ_{ab} along the chain directions is 10^{-4} Ω cm with anisotropy $\rho_c/\rho_{ab} \sim 10^2$. The temperature dependence of ρ_{ab} appears to be a simple power law, $\rho_{ab} \propto T^n$, with n varying between 1 and 3 and with no indication of residual resistivity at $T \sim 1.4$ K. The measured ratio $\rho_{ab}(300\text{ K})/\rho_{ab}(1.4\text{ K})$ is about 3000.

Near 4 K, the c-axis resistivity drops abruptly more than 3 orders of magnitude, apparently to zero, while ρ_{ab} is continuous. Magnetization measurements by Spal *et al.*[3] have also revealed an anisotropic superconductivity—the flux expulsion depends strongly on the orientation of the applied field with respect to the crystalline axes confirming the anisotropic behavior first observed in the transport measurements. An additional unusual feature is that the temperature dependence of the flux expulsion is not a step function but rather a continuously increasing function for $T < T_c$. Furthermore, $4\pi M/H$ is field dependent even at fields less than 10^{-4} of the thermodynamic bulk critical field.

A recent transport study[4] revealed enhanced magnetoresistance which has been attributed to the unusual Fermi surface which results from the perpendicular sets of relatively weakly coupled linear chains. A logarithmic dependence of

$$\frac{\Delta\rho(H)}{\rho(0)} \propto H^2 \ln\left[\frac{H_0}{H}\right]$$

for $H < H_0$, where H_0 is a characteristic effective field, has been found experimentally in agreement with theory.[4]

The interpretation of the superconducting state in this crystal has been a controversial issue,[5,6] principally because of the close proximity of the upper transition temperature to that of free Hg. Moreover, neutron scattering studies have shown that on cooling from 298 to 10 K about 1% of the Hg atoms continuously leave the chains and reversibly reenter the chains as the crystal is warmed back to 298 K.[7]

The structural studies[8] indicate that there are Hg chains only along the a,b directions. At room temperature, they are randomly phased and incommensurate with the three-dimensional (3D) host lattice of the AsF_6 octahedra. The Hg chains are stiff (Debye temperature $\Theta_D^{1D} \sim 700$ K) with a Hg-Hg distance which remains almost temperature independent, while the host AsF_6 lattice is relatively soft ($\Theta_D^{3D} \sim 70$ K). Consequently, on cooling, about 1% of the Hg atoms leave the chains, either dispersed in the crystal or extruded onto the ac and bc surfaces. However, x-ray fluorescence spectroscopy studies of the surfaces of the crystal at various temperatures lead to the conclusion that if Hg were extruded to the surface the film thickness would be less than 500 Å.[6] This sets an upper limit of 0.001% Hg on the surface and rules out the suggestion of Datars *et al.*[5] that the anisotropic superconductivity is a result of the extruded Hg on the surface. Detailed analysis of the electrical transport data demonstrates definitively that superconductivity cannot arise from a semicontinuous surface film of Hg. We conclude that most of the Hg atoms which leave the chains on cooling are atomically dispersed throughout the solid (possibly in the volume available from the 6% AsF_6^- vacancies).[10]

In spite of the extensive experimental and theoretical[11] studies of the $Hg_{3-\delta}AsF_6$ compound, the understanding of the superconductivity in this crystal and, in particular, of its anisotropic behavior, are far from being complete. In this paper we report our recent study of the pressure and temperature dependence of the susceptibility χ at pressure and temperature ranges of 0—14 kbar and 0.3—4.2 K, respectively. A study of the effect of pressure (0—4 kbar) on the upper transition temperature to the anisotropic state was conducted simultaneously by Schirber *et al.*[12] They found, in agreement with our findings, that the superconducting properties of the crystal near 4 K track those of the elemental α and β mercury phases. Thus the elemental mercury within the crystal may be the source for the superconducting transition near 4 K. Our investigation was done over an extended pressure and temperature region which includes the lower transition tempera-

ture where the crystal becomes an isotropic superconductor. In Sec. II we describe the experimental techniques that have been employed in measuring χ at high pressures. In Sec. III we describe the experimental results and discuss their consequences in terms of various physical mechanisms which may be responsible for the unusual superconducting properties in this exotic material.

II. EXPERIMENTAL TECHNIQUES

The magnetic susceptibility has been measured by a Hartshorn mutual inductance bridge. The circuitry is similar to the bridge that was previously used for studying the magnetoresistance at low fields.[4]

The high pressures have been obtained in a Teflon high-pressure cell, where fluorinert[13] liquid was used as a pressure medium. The Teflon cell is confined in a self-clamped high-pressure "bomb" made of a nonmagnetic hardened Be-Cu alloy.

After creating the desired pressure level in the cell, the bomb is quickly transferred from the press to the ^{3}He cooling system. It is thermally anchored onto the bottom of the ^{3}He pot of the measuring probe. The whole ^{3}He probe is then initially cooled by inserting it into liquid nitrogen. Upon reaching a temperature of nearly 77 K, it is transferred to the ^{3}He cooling cryostat for the continuation of the cooling down to 0.3 K. The duration of the first and second cooling states are approximately 2 and 4 h, respectively.

A special measuring procedure for obtaining the susceptibility at high pressure has been employed. In order to enhance the sensitivity, we have inserted the coils of the bridge into the high-pressure cell, rather than winding them in the conventional way, outside of the high-pressure bomb. A special miniature set of coils which contains the primary and the two oppositely wound secondary coils of 1000 turns was constructed in a cylindrical shape, sized 8 $\times$ 6 mm^2 in diameter. By employing this method, we have achieved a satisfactory filling factor and thus a significant enhancement of the sensitivity to the sample susceptibility.

Since it is impossible to remove and to reinsert the sample from the bridge for the determination of the net value of the off-balance signal, we have developed a special *in situ* calibration procedure for both the susceptibility and the internal pressure readings. This is accomplished in the following way. First, we have used powder samples that were prepared from single crystals that were ground shortly prior to loading the sample into one of the equivalent secondary coils. This eliminates eddy currents, thereby nullifying the resistive component R due to the sample. Second, we have used a small piece of pure Sn foil which was placed inside the second equivalent secondary coil and was kept there during all our experiments. The signal due to the Sn specimen at the superconducting phase transition, at $T_c \simeq 3.7$ K, is comprised of a pure inductive L signal. It was used for establishing a convenient scale for the conversion of the bridge signals, due to the sample, to susceptibility values. This was simply obtained by comparing the bridge signal due to the mercury chain compound at temperature $T=0.3$ K and ambient pressure (where maximum bulk susceptibility $-4\pi M/H=1$ is obtained) to the signal obtained due to the Sn superconductor. This established the scale for the bridge signal that was subsequently used for the results obtained at any temperature and pressure. In addition, the internal pressure values were determined by measuring the shift of the superconducting transition ΔT_c for the Sn sample in the cell.[14] Corrections for demagnetization effects were applied to the raw data by assuming a demagnetization factor of a spherically shaped sample.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The results of the temperature dependence of the susceptibility of the $Hg_{3-\delta}AsF_6$ crystal at various constant pressures is shown in Fig. 1. At pressures $p>0$, two sharp transitions are seen prior to the gradual increase of the diamagnetic susceptibility. These are a sign of the existence of free mercury that is separated by the applied pressure into the α and β mercury phases.[15] Comparing the values of χ of these sharp steps to the maximum susceptibility χ_m obtained at $T=0.3$ K and $p=0$, which correspond to a total flux exclusion, we find their contribution to be between 0.4% to 1.5% of χ_m. The identification of the α and β phases[16] is based on the observed phase line contour that those transitions exhibit in the temperature-pressure phase space. The second and most important result of our experiments is the shift of both transition temperature T_c^{I} and T_c^{II} toward zero temperature as a function of increasing pressure values.

The two sharp transitions in χ are not an intrinsic property of the crystal. Given the extreme sensitivity of the compound to decomposition, the free Hg may result from imperfect sample handling. In more carefully handled samples, which were measured at zero pressure where no

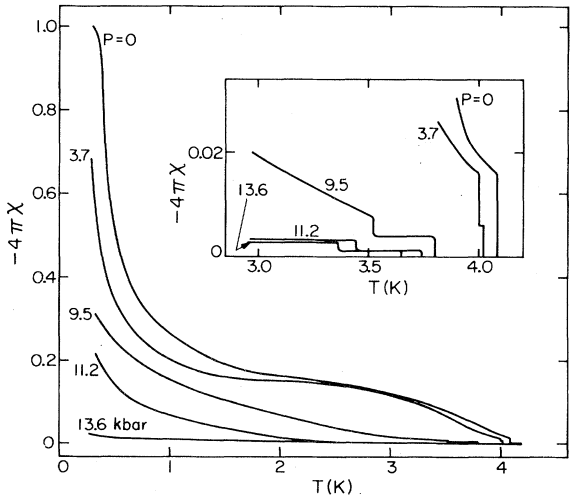

FIG. 1. Temperature dependence of the magnetic susceptibility of $Hg_{3-\delta}AsF_6$ at various pressures. The inset indicates the dependence of the superconducting transition temperatures of the α and β mercury at the various pressures. The indicated pressure values are in units of 10^3 bar.

pressure fluid medium is required to be in direct contact with the ground sample having a large surface-to-volume ratio, no such sharp transitions are observed.[3] Moreover, in repeated temperature scans of χ in different samples at the same applied pressure, the shape and magnitude of the susceptibility curves are independent of the values of the small sharp steps.

The gradual increase of χ following the sharp transition is attributed to an intrinsic property of the mercury chain crystal. Between the two transition temperatures at zero pressure, $T_c^{\mathrm{I}}=4.1$ K and $T_c^{\mathrm{II}}=0.4$ K, corresponding to the temperatures where a sharp drop in the resistivity along the c axis occurs and the one where a full flux exclusion is achieved, respectively, the crystal is in an anisotropic superconducting state. At this state, zero resistivity is observed only along the c axis which is perpendicular to the chain directions. Meissner-effect studies revealed anisotropic behavior as well.[3] The ratio of the susceptibilities measured with fields along the a,b axis and the c axis, $\chi_{a,b}/\chi_c$, increases as the field is reduced and it is as large as 17 in $H=0.015$ G near $T=3.5$ K and $p=0$. At $T_c^{\mathrm{II}}\simeq 0.4$ K, the measured susceptibility corresponds to a complete flux exclusion, $4\pi\chi=-1$, and the crystal reaches an isotropic superconducting state.

Spal *et al.*[6,10] suggested that the anisotropic superconductivity results either from the proximity effect driven by the dispersed Hg in contact with the anisotropic $Hg_{3-\delta}AsF_6$ or possibly from intrinsic interchain coupling. Both of these possibilities are remarkable, the former due to the high degree of the reproducibility of the experimental results in different samples. These results should be critically dependent on the dimensions and the morphology of the dispersed Hg microscopic inclusions in each sample that comprise the inner superconducting network. The latter possibility is also esoteric since superconductivity is basically a macroscopic quantum phenomenon and it is difficult to conceive of a situation of an intrinsic anisotropic superconductivity where the current is nondissipative only along one crystal axis.

While, based on our experimental findings, we cannot rule out the second possibility, we find the first one to be consistent with our results. In this interpretation, the upper transition temperature to the anisotropic superconducting state is the result of the Hg inclusions which are developed inside the crystal. Their form and distribution must be such that a percolation threshold is established *only* along the c-axis direction.[17] In this case, the effect of pressure on the upper transition temperatures T_c^{I} of $Hg_{3-\delta}AsF_6$ would be due to the decrease of the critical temperature of the elemental Hg comprising the microscopic inclusions. Thus the transition temperature of the superconductivity which results from the coupling of the elemental Hg inclusions with the rest of the crystal, via the proximity effect, is also depressed.

The effect of the external pressure on the lower transition temperature T_c^{II}, which is the "intrinsic" superconductivity of the mercury chain compound, is perhaps more intriguing. Rice[18] suggested that the superconductivity in $Hg_{3-\delta}AsF_6$ below 0.4 K may be an example of triplet superconductivity. Generally, it is known from theoretical studies[19] that depending on the magnitude of the backward scattering amplitude g_1 and the forward scattering amplitude g_2 a quasi-one-dimensional metal can be in one of four main phases in g_1-g_2 phase space: singlet (BCS) superconductivity, triplet superconductivity, Peierls phase (charge-density wave), and antiferromagnetic (spin-density wave) phase. The energies of all the four phases are very close together, so that minor perturbations can cause changeover from one phase to another. Such perturbations are interchain Coulomb coupling, umklapp scattering, etc. Pressure can modify these parameters and induce crossover from one phase to another in g space, as has been demonstrated experimentally for $(TMTSF)_2PF_6$ [tetramethyltetraselenafulvalene (TMTSF)].[19]

Pairing with nonzero spin in layered and quasi-one-dimensional superconductors was considered by Efetov and Larkin.[20] They have shown that for systems with a physical separation between close-by electrons, such as the dichalcogenide layer compounds, triplet superconductivity is possible, since the physical separation implies a vanishing of the wave function between the layers, or parallel chains, favoring an antisymmetrical spatial wave function and thus a triplet spin state. This argument holds here as well.

Gutfreund and Little[21] showed that while *backward* non-spin-flip scattering is unfavorable for triplet superconductivity (as is well known for 3D metals), *forward* scattering does not interfere with it, while it suppresses the Peierls state. The large number of anion vacancies in $Hg_{3-\delta}AsF_6$ ($\sim 6\%$) causes appreciable forward scattering but not backward scattering as is indicated by the large mean free path ($\sim 10\ \mu$m). This feature may also be consistent with a superconducting state where triplet coupling is favored.

The phonons involved must be interchain phonons which couple electrons on different chains. The frequency of such phonons is strongly pressure dependent,[22] and it should increase with increasing pressure. This effect modified the electron-phonon coupling constant λ, which varies inversely as the square of the frequency. Thus any tendency to triplet superconductivity must be strongly suppressed by the pressure, consistent with the observations reported above.

IV. CONCLUSIONS

In conclusion, we have seen that high pressure applied to $Hg_{3-\delta}AsF_6$ separates the superconductive transition temperatures due to the different component in this system: the α and β free mercury which result from sample degradation and the two "intrinsic" transitions. Both of these latter transitions are found to be suppressed by pressure. The upper transition T_c^{I} is interpreted as due to the formation of a superconducting network of regions comprised of elemental Hg inclusions coupled to nearby portions of the crystal via the proximity effect in a way that a percolation threshold is obtained only along the c-axis direction. The origin of this remarkable anisotropy is not understood. The reduction of T_c^{I} with increasing the pressure follows the change in the critical temperatures of the elemental Hg inclusions.

The effect of the pressure on the lower transition is

found to be consistent with the possibility of triplet superconductivity. The applied pressure modifies the frequencies of the interchain phonons which couple electrons on different chains. This in turn modifies the electron-phonon coupling and suppresses the transition temperature.

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