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Brief Reports

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Role of elemental mercury in the superconductivity of $Hg_{3-\delta}AsF_6$

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Pressure-temperature excursions necessary for conversion of rhombohedral α-Hg to body-centered tetragonal β-Hg have been applied to single crystals of $Hg_{3-\delta}AsF_6$. The superconducting properties of the compound near 4 K are shown to track those of elemental α- and β-Hg which appear to be trapped within the sample.

There has been a good deal of controversy concerning the nature of the superconductivity near 4 K of the incommensurate linear-chain compound $Hg_{3-\delta}AsF_6$. The observation of anisotropic superconductivity by Spal *et al.*[1,2] near 4 K has been interpreted by Datars *et al.*[3] as due to free Hg, perhaps that extruded from the crystals upon temperature cycling. This extrusion is due to the relatively small contraction of the incommensurate Hg chains compared to that of the AsF_6 lattice and has been observed by Pouget *et al.*[4]

Elemental Hg undergoes a phase change with pressure first observed by Bridgman[5] at about 12 kbar and 200 K from a simple rhombohedral phase to a body-centered tetragonal modification which is the stable form below 79 K even at zero pressure. This phase change is probably martensitic in character[6] and displays a great deal of hysteresis, but temperature-pressure-time cycles were empirically determined which result in the formation and retention of β-Hg at low temperature. The pressure-temperature phase diagram is shown in Fig. 1, but it is emphasized that, at low temperatures, time is an important parameter.

The electronic properties of the two phases differ substantially. β-Hg has a resistivity 1.7 times that of α-Hg at 77 K. The superconducting transition temperatures T_c, superconducting critical fields, and pressure dependences of T_c are 4.152 vs 3.949 K, 412 vs 339 G, and 0.037 vs 0.048 K/kbar for α and β, respectively.[7] This unique behavior of Hg provides an excellent means of determining the extent of involvement of elemental Hg in the superconductivity near 4 K of $Hg_{3-\delta}AsF_6$. This study indicates that elemental mercury within the sample is the source of the superconductivity near 4 K.

The superconducting transitions were determined

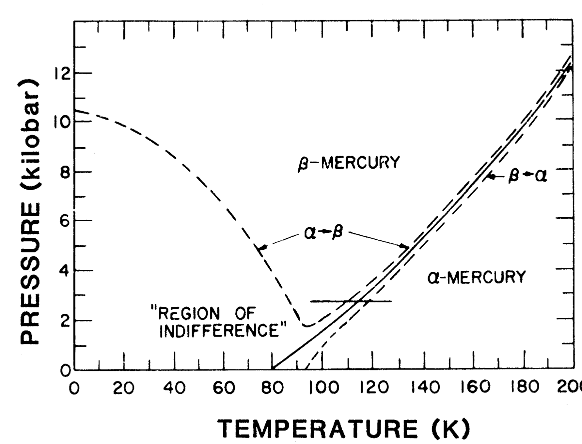

FIG. 1. Phase diagram of solid mercury. The region between the dashed lines (the region of indifference) represents the temperatures and pressures where either phase may exist. The solid horizontal line indicates the lowest pressure (2700 bars) at which it was found possible to produce pure β-Hg by slow cooling under a truly hydrostatic pressure.

by measurement of the change in inductance detected with a General Radio inductance bridge in conjunction with a lock-in detector operated at 100 Hz. Temperatures were measured with a Lake Shore cryogenics thermometer calibrated against the vapor pressure of He. de Haas–van Alphen frequencies were obtained using the field modulation technique[8] in fields up to 55 kOe. Pressures were generated in fluid or solid He.[9]

Samples were single crystals grown at the University of Pennsylvania[10] which were of sufficient quality to display large de Haas–van Alphen signals. After pressure-temperature cycling, the first sample showed a small fairly sharp superconducting transition at 4.15 K followed by a much broader transition beginning 0.1– 0.2 K lower in temperature (see Fig. 2, trace e). The sharper transition is attributed to free mercury, not detected in the as-received sample (trace a). This free Hg signal was found to increase in size during the cycling of pressure and temperature described below. We attribute this at least partially to cryopumping of moisture from the gaseous He pressure system which, in our initial runs, we did not cold trap. The second single-crystal sample was used in magnetic measurements and its superconductivity was monitored via the critical field[6] at 1.1 K.

Transformation of α- to β-Hg is very sluggish at liquid-nitrogen temperatures and below. Several

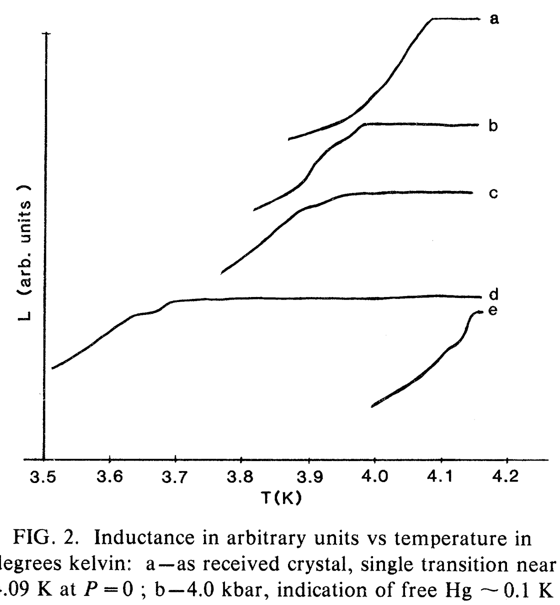

FIG. 2. Inductance in arbitrary units vs temperature in degrees kelvin: a—as received crystal, single transition near 4.09 K at $P=0$; b—4.0 kbar, indication of free Hg ~0.1 K above broad transition which is shifted ~0.15 K to lower temperature by the 4 kbar; c—after $\alpha \rightarrow \beta$ transition procedure at $P=0$, free β-Hg step at 3.95 K with broad transition ~0.1 K lower in temperature; d—4.0 kbar in β phase, both transitions are shifted ~0.2 K in keeping with the larger pressure derivative of T_c for β-Hg; e—after raising temperature above 100 K, $P=0$, now have substantial free Hg transition at 4.15 K.

hours at 4 kbar and near 100 K resulted in transformation of only part of the Hg so the sample was held near 100 K for the order of 12 h at 4 kbar resulting in full conversion. Upon completion of this recipe for conversion of α- to β-Hg, we observed that both the sharp "free" Hg signal and the broader "compound" signal were depressed about 0.20 K at zero pressure, exactly (within our experimental uncertainty of about 0.005 K) the difference in the critical temperatures of α- and β-Hg of 4.152 and 3.949. At 4 kbar there was a further depression of ~0.2 for both transitions (see Fig. 2, traces c and d). This change is expected from the known value of dT_c/dP for β-Hg. Thus we have two signatures for the β phase, the value of T_c and its pressure derivative.

After warming the sample to ~100 K and returning to low temperatures (at zero pressure), the superconducting transitions return to their previous values of 4.15 and ~4.05 K (Fig. 2, trace e). At 4 kbar (Fig. 2, trace b) both transitions are depressed ~0.15 K consistent with the smaller pressure derivative of α-Hg than that of β-Hg. Again we have the double signature of T_c and its pressure derivative for α-Hg. These observations coupled with the transformation behavior from α- to β-Hg leave little doubt that the superconductivity near 4 K is closely linked to elemental Hg. To summarize, in Fig. 2 we show reproduction of the inductance (in arbitrary units) versus T in the sequence from as received, at 4 kbar in α phase, after transition to β-Hg at zero pressure, in β phase at 4 kbar, and finally back to the α phase.

The second sample was studied entirely in magnetic fields and was oriented with its c axis along this applied field. Strong de Haas–van Alphen (dHvA) signals could be observed even with the pickup coils completely outside the $\frac{1}{8}$-in. i.d. by $\frac{3}{8}$-in. o.d. BeCu pressure vessel. This observation indicates that the sample was of high perfection. Five sets of frequencies could be detected in good quantitative agreement with the values given by Razavi *et al.*[11] Pressure derivatives were determined for several of these frequencies which are in satisfactory agreement with the values obtained by Batalla *et al.*[12] Since a comprehensive study of the pressure dependence of the Fermi surface of $Hg_{3-\delta}AsF_6$ was under way at McMasters, our determinations were primarily to insure that we were looking at the same materials and as a test for the quality of our single crystal.

We were, however, interested in ascertaining what would happen to the Fermi surface upon transformation of the Hg in the system to β-Hg. Since β-Hg is ~1.5% smaller volume than α-Hg, it was expected that not much damage might occur upon going from α to β but that the lattice might be disrupted on the reverse transformation. Instead we observed a *complete* loss of dHvA signal after transformation to the β phase, indicating a large increase in electron scattering. The superconducting state of the compound was monitored in this experiment by observation of the critical field H_c at 1.1 K. The values for α- and β-Hg are 380 and 314 G, respectively, so there is no difficulty in detecting the transition. Transformation back to α resulted in recovery of the strongest oscillations but the sample was obviously severely damaged. Subsequent examination of the sample showed it had broken into several fragments and free Hg droplets were discernible.

We take these observation of the loss of the dHvA signal and the damaging of the crystal as further evidence that "bulk" Hg exists within these single-crystal samples in spite of their perfection as far as electronic scattering is concerned. Transforming this included Hg to the β phase severely strains the lattice and cycling back and forth ultimately results in comminution of the single-crystal sample.

In summary, these results strongly indicate that bulk Hg in the crystal dominates the superconductivity of $Hg_{3-\delta}AsF_6$ near 4 K. This possibility was discussed by Spal *et al.*[2] and might lead to the anisotropic superconductivity via some proximity effect. It is clear that the mercury in the chains themselves is not giving rise to this superconductivity because there is no way imaginable that these one-dimensional chains (as evidenced by the observed planar Fermi surfaces) could undergo the three-dimensional crystallographic phase change inferred from our data. It is also clear that it is not free Hg on the surface of the crystal or exterior to the crystal because we can see the signature of this component as a separate, sharper transition which becomes more dominant as the sample deteriorates, freeing Hg.

The broadness of the transition occurring at a temperature 0.1– 0.2 K below that of the unconfined Hg may indicate that this Hg is constrained by the compound lattice by a range of effective pressures greater than 2– 4 kbar. Our results give no insight as to whether this Hg is in the AsF_6 vacancies or aligned in such a way to give rise to the observed anisotropies of the superconducting properties. It would be of considerable interest to see whether similar behavior is observed in the sister compound $Hg_{3-\delta}SbF_6$ and as yet not synthesized cogeners with Pf_6, ClO_4, and similar anions.

ACKNOWLEDGMENTS

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