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Mercury Extrusion from Linear-Chain Mercury Compounds

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Evidence is presented from differential thermal analysis to show that mercury is extruded from the linear-chain mercury compounds $Hg_{2.86}AsF_6$ and $Hg_{2.91}SbF_6$ when cooled below 200 K. The anisotropic superconductivity observed recently in $Hg_{2.86}AsF_6$ is shown to result from extruded mercury.

A series of recent observations in the linear-chain mercury compound $Hg_{2.86}AsF_6$ have been interpreted as evidence of anisotropic superconductivity.[1,2] Although the critical temperature and critical magnetic field are very similar to those of pure mercury, it was considered improbable that metallic mercury is the source of such an extremely anisotropic and temperature-dependent effect. We report in this Letter the results of differential thermal analysis (DTA) of the linear-chain mercury compounds $Hg_{2.86}AsF_6$ and $Hg_{2.91}SbF_6$ which demonstrate the presence of metallic mercury at low temperatures. This mercury is extruded from the compounds when they are cooled below 200 K and is reincorporated into the compounds upon warming. The observed superconductivity in $Hg_{2.86}AsF_6$ is due to the extruded mercury and the observed anisotropy and temperature dependence follow naturally from our model of mercury extrusion.

The room-temperature crystal structure of both linear-chain mercury compounds consists of linear, nonintersecting mercury chains in a tetragonal array of AsF_6^- or SbF_6^- octahedra.[3] The mercury chains are situated in nonintersecting channels parallel to the a and b axes and are incommensurate with the three-dimensional host lattice. Short-range ordering along the mercury chains appears below 200 K.[4] Other measurements indicate that there is a change near 200 K in the coefficient of thermal expansion,[5] electrical resistivity,[6] thermoelectric power,[7] magnetic susceptibility,[8] and nuclear-magnetic-resonance relaxation time[9] and suggest the possibility of changes in the mercury chains or host lattice with temperature. The present work was undertaken to study these changes with the help of differential thermal analysis.

In DTA experiments, the difference in temperature between a sample and reference is measured as the temperature of their environment is varied at a continuous rate. The temperature of the sample depends upon the amount of energy absorbed or released by it. If, for example, upon warming the sample undergoes a phase transition at which latent heat is absorbed, the temper-

ature of the sample drops relative to that of the reference. This results in a minimum in the difference in temperature as a function of time or temperature.[10] In the present experiments, the sample temperature was measured with a copper-Constantan thermocouple embedded in crystallites of the mercury compounds sealed in a quartz tube. The reference thermocouple was in an evacuated quartz tube. Both tubes were in a copper block which could be heated or cooled at a continuous rate. The rate of change of temperature was typically 10 K/min during warming and 8 K/min during cooling cycles.

Typical DTA curves for $Hg_{2.91}SbF_6$ and $Hg_{2.86}AsF_6$ are shown in Figs. 1 and 2, respectively. There is a broad peak during cooling between 205 and 185 K in the temperature range of the changes detected previously.[4-9] The warming curves show no change between 185 and 205 K but exhibit a sharp minimum at 235 K superimposed on additional structure between 220 and 240 K. The cooling peak is observed only if the sample is cooled from at least 240 K and minima in the warming curve occur only if the sample is warmed from a temperature of 200 K or less. The dependence of warming curves on the temperature to which the sample is cooled before starting the warming cycle is illustrated in Fig. 2. Here, as the starting temperature of the warming curve is lowered from 201 to 184 K, the amplitude of the warming signal increases. The signal is quite insensitive to the starting temperature of the warming cycle for starting temperatures below 180 K. The above properties of the DTA curves are common to all samples of both compounds. The de-
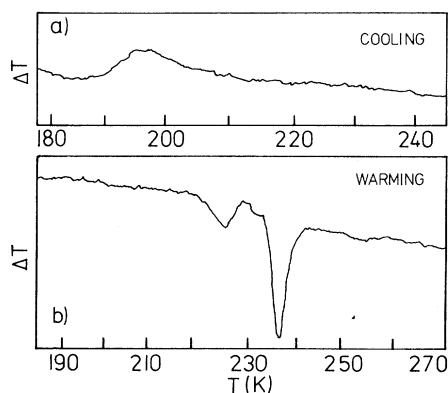
tailed shape of the warming curves is different for the two compounds (compare Figs. 1 and 2) and varies somewhat from sample to sample. The DTA curves are independent of the heating or cooling rate for rates between 3 and 24 K/min. They are also independent of the length of time the sample is held at a temperature before commencing the warming or cooling cycle for times between several minutes and several days. The DTA response of pure mercury, used as check of the apparatus, showed a peak due to freezing during cooling and a minimum of similar magnitude due to melting during warming. Both changes occurred at 235 ± 5 K.

The minimum at 235 K, the melting point of mercury, in the DTA warming curves is taken to be direct evidence of the presence of free mercury that is extruded from the compounds during cooling. The amplitude of the minimum at 235 K, and thereby the amount of mercury extruded, increase as the temperature to which the sample is cooled decreases from 200 to 180 K. It is estimated from the area under the melting minimum that, after cooling to 180 K, between 0.5 and 5 at.% of the mercury of the compounds is extruded, the amount varying from sample to sample. We propose that the mercury is extruded to those sample surfaces where mercury channels end and form a deposit consisting of a semicontinuous thin film and droplets. The droplets have been observed visually by the present authors and by Wei et al.[8]
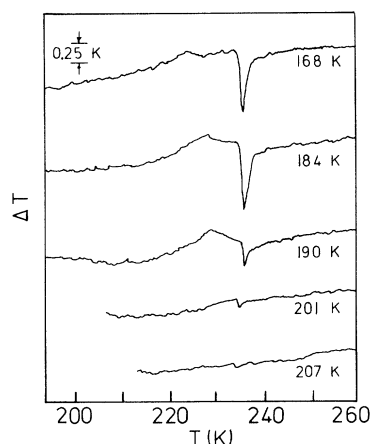

FIG. 1. Difference in temperature, $\Delta T = T_{sample} - T_{ref}$, between a sample of $Hg_{2.91}SbF_6$ and a reference thermocouple vs sample temperature during (a) cooling and (b) warming cycles of differential thermal analysis.

FIG. 2. Dependence of the difference in temperature, $\Delta T = T_{sample} - T_{ref}$, vs sample temperature during warming cycles of differential analysis of $Hg_{2.86}AsF_6$ for different temperatures to which the sample was cooled before starting the warming cycle.

Our model of mercury extrusion implies that no mercury is deposited on a sample surface that is parallel to the a-b plane. Evidence of this appears in the observed[1,2] anisotropic superconducting properties. Measurements of the resistivity ρ_c along the c axis show a superconducting critical temperature of 4.1 K and a critical field of 380 G at 1.4 K, very close to the values for free mercury. However, the resistivity in the a-b plane varies continuously down to 1.4 K. This anisotropy is explained by the placement of the electrical probes relative to the extruded mercury. When the probes are on a crystal face on which there is mercury, superconducting paths through the mercury short out the sample below 4.1 K. When probes are on the a-b surface for measurement of ρ_{ab}, there is no free mercury between the probes, and the normal resistivity of the material is observed. The anisotropy of the flux exclusion that has been observed[2] also results from the anisotropic geometry of the mercury deposit. When the magnetic field is parallel to surfaces covered with mercury ($\vec{H} \parallel \hat{c}$), the flux exclusion is minimal. For $\vec{H} \perp \hat{c}$, the observed flux exclusion is an order of magnitude larger, corresponding to a larger projection of the area of the mercury films onto the plane perpendicular to $\vec{H}$. The temperature and magnetic field dependence of $-4\pi M/H$ results from flux penentration in the mixed state of a thin film and are similar to previous observations on small particles and thin films.[11-13]

An important feature of the extrusion is the hysteresis shown in Fig. 1. The DTA warming curves indicate that the reabsorption of the mercury starts at 220 K and occurs, to a major extent, only after the mercury is melted at 235 K, i.e., at a temperature 40 K higher than the extrusion temperature. The reabsorption is complete in the DTA experiments since no evidence of freezing mercury is detected upon cooling. Absorption of liquid mercury is also the process by which the compound is grown at 250 K.[3] The extrusion takes place in the temperature range where a transition is suggested by other properties of linear-chain mercury compounds.[4-9] In particular, the coefficient of thermal expansion along the a and b axes drops at 200 K from 7.6×10^{-5} K^{-1} to 1.0×10^{-5} K^{-1} while the same coefficient along the c axis remains unchanged (6.5×10^{-5} K^{-1}).[5] In neutron scattering experiments,[4] a short-range order which is not present at room temperature has been observed at 180 K, but no structural transition has been reported at the ex-

trusion temperature. Hysteresis resembling that in the DTA results has not been observed in previous experiments on linear-chain mercury compounds.

The question then arises: In what way is the mercury distributed in the crystal before it is extruded from the linear channels to the sample surface? Without any mercury appearing at the surface during cooling from room temperature to 210 K, the lattice parameter contracts continuously by 0.7% while the mercury-mercury distance within a chain remains constant.[5] It seems necessary to assume that, rather than having the ends of the mercury chains "protruding" beyond the lattice, mercury chains are shortened by mercury being placed into defect positions. The discrepancy[3] between the stoichiometric formula Hg_3AsF_6 determined from chemical analysis and the structural formula $Hg_{2.86}AsF_6$ also suggests that some mercury, as much as 5 at.%, is not in the chains. This amount is the same as the upper estimate of the amount of mercury extruded during the DTA measurements. A small amount of mercury in defect positions at helium temperatures has been discussed as a possible cause of the unusually large linear term in the specific heat.[8]

Mercury extrusion and the other properties of the compounds are consistent within the following model. The reduction of the thermal expansion coefficient[5] below 200 K, implying an increased rigidity in the a-b plane, and the short-range order[4] both correspond to an interaction between parallel chains. This interaction appears to be weak above 200 K, i.e., in the disordered state, so that the translational invariance of the incommensurate mercury chains results in a large number of possible defect configurations. As short-range order sets in, the corresponding configurational entropy and, along with it, the occupation of such defect positions are reduced. Mercury from these positions goes into the chains and forces excess mercury out of the ends of the channels resulting in mercury extrusion. Extruded mercury forms droplets because a relatively large amount of extruded mercury cannot be deposited as only a thin film on an uneven surface. The hysteresis of the reabsorption can then be described by assuming that the redistribution of the mercury from the droplets to the channel ends where it can be absorbed is only possible in the liquid state.

In summary, differential thermal analysis of $Hg_{2.86}AsF_6$ and $Hg_{2.91}SbF_6$ reveals the presence

of free mercury which is extruded from the compounds when cooled below 200 K and is reincorporated into the compounds during warming. A model is presented of an anisotropic extrusion process which is consistent with many properties of the linear-chain mercury compounds observed near 200 K and also give a simple explanation for the anisotropic superconducting properties observed below 4.1 K.

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Fast-Time Heat Capacity in Amorphous SiO$_2$ Using Heat-Pulse Propagation

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We have performed heat-pulse propagation measurements in amorphous SiO$_2$ over the temperature range 50 mK to 3.8 K on the submicrosecond time scale (some two to three orders of magnitude faster than previous measurements). No evidence for deviations from the dc heat capacity have been observed at low temperatures. Between 1 and 2 K, we see evidence for "ballistic" phonon propagation, induced by saturation of the scattering centers.

Recently there has been considerable interest in the thermal and transport properties[1,2] of amorphous dielectrics. To explain the "universal behavior" of many different materials a model was proposed by Anderson, Halperin, and Varma[3] and by Phillips[4] in which tunneling between localized two-level systems in the glass resulted in a distribution of low-lying states contributing both to the heat capacity and to the scattering of phonons. Very recent ultrasonic measurements[5,6] have beautifully confirmed some of the predictions of this model while they have also pointed out some problems. Specifically, because

of the wide range of tunneling probabilities available in such a model, the relaxation time for a given energy splitting varies widely for different states and the measured specific heat of such a system should depend on the time scale of the measurement. The specific heat is of the form[2]

$$C = C_1 T + C_3 T^3 \quad (0.1 \text{ K} < T < 2.5 \text{ K}) \qquad (1)$$

and its has been shown that C_1 should have a time dependence $C_1(\tau) \propto \ln(4t/\tau_m)$, where τ_m is a relaxation rate for tunneling states[7] which is 0.46 μsec at 0.1 K for SiO$_2$.

From the ultrasonic absorption measurements