Superconductivity of Hg_3NbF_6 and Hg_3TaF_6

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Low-temperature ac susceptibility measurements show that two new metallic compounds, Hg_3TaF_6 and Hg_3NbF_6, are superconductors with a critical temperature of 7.0 K. Critical fields are 20% higher in Hg_3TaF_6 but the temperature dependence of the critical field of the compounds is very similar down to 1.35 K. The critical field extrapolated to $T=0$ K is 0.17 T for Hg_3TaF_6 and 0.13 T for Hg_3NbF_6.

I. INTRODUCTION

Recently, two new isostructural mercury compounds, Hg_3NbF_6 and Hg_3TaF_6, have been prepared.[1] Crystals of the compounds have a silver, metallic appearance and are in the form of small, very thin, soft platelets. The crystals are characterized by layers of hexagonally close-packed NbF_6 or TaF_6 octahedra separated by hexagonal close-packed sheets of mercury atoms. The mercury layers are in the form of a regular hexagonal net of mercury atoms rotated 30° about [001] from the axis of the NbF_6 or TaF_6 hexagonal net. The close-packed spacing determined by the x-ray analysis shows that there are three Hg atoms for every octahedron.

A test for superconductivity is the first physical measurement of these compounds after the x-ray-diffraction study.[1] The purpose of this paper is to report the results of these experiments which show that the compounds are superconductors with a critical temperature of 7.0 K. The temperature dependence of the critical magnetic field is also reported.

II. EXPERIMENTAL

The compound Hg_3NbF_6 was prepared by first purifying NbF_5 by sublimation in a dry plastic tube under vacuum. This was then reacted with the exact stoichiometric amount of HgF_2 in SO_2 in a sealed ampoule to form a solution of $Hg(NbF_6)_2$. The solution was filtered on to mercury and left to react with it for several days. The solution slowly changed color to orange with formation of thin, silver plates of Hg_3NbF_6. The preparation of Hg_3TaF_6 was similar to that of Hg_3NbF_6 except that white needles also formed in the first few hours of the reaction. They dissolved in SO_2 after a few days.

Small crystalline, metallic platelets were isolated from solution. Approximately 70 mg of small crystals were sealed in a Kel-F sample holder for experiments. A single platelet of Hg_3NbF_6 with approximate dimensions $2\times1\times0.3$ mm^3 was also used. It probably consisted of several crystals and became slightly bent during handling because of the soft nature of the material.

The ac susceptibility was measured with the sample in one of a balanced pair of coils which picked up signal from a modulation coil driven at 107 Hz. The ac signal from the balanced pair to that from one coil was 1:5000. The signal was detected with a lock-in amplifier whose output was displayed on a strip-chart recorder.

The temperature was changed at a constant rate above 4.2 K by warming the coil and sample with a resistance heater after they had been cooled with a small amount of liquid helium. The temperature was measured with a carbon-resistor thermometer calibrated with liquid helium at atmospheric pressure and the superconducting transition of lead put in the place of the sample. The temperature was then obtained from a two-parameter logarithmic formula. Temperatures between 4.22 and 1.35 K were controlled by boiling liquid helium and were determined from the vapor pressure measured with a Texas Instruments pressure gauge.

The magnetic field was supplied by a 12-in. electromagnet. It could be set to zero magnetic field for measurements of critical temperature.

III. RESULTS

Measurements of the differential magnetization exhibited transitions as a function of temperature and are shown in Fig. 1. The superconducting transition of lead with a critical temperature of 7.193 K occurs over a very narrow temperature range and serves as a reference temperature. The transitions of microcrystalline Hg_3TaF_6 and Hg_3NbF_6 are very similar. The critical temperatures taken at 90% completion during increasing temperature are the same within the uncertainty of measurement of 1%. The critical temperature for both compounds is 7.0 ± 0.1 K, where the error includes uncertainties in temperature calibration and possible differences in temperature between the sample and thermometer. The temperature difference between 10% and 90% of the transition is 0.6 K for Hg_3TaF_6 and 0.3 K for Hg_3NbF_6. The transition in Fig. 2 for the single platelet of Hg_3NbF_6 is essentially the same as that in Fig. 1 for the microcrystals for Hg_3NbF_6: The critical temperature is 7.0 K and the difference between 10% and 90% of the transition is 0.3 K.

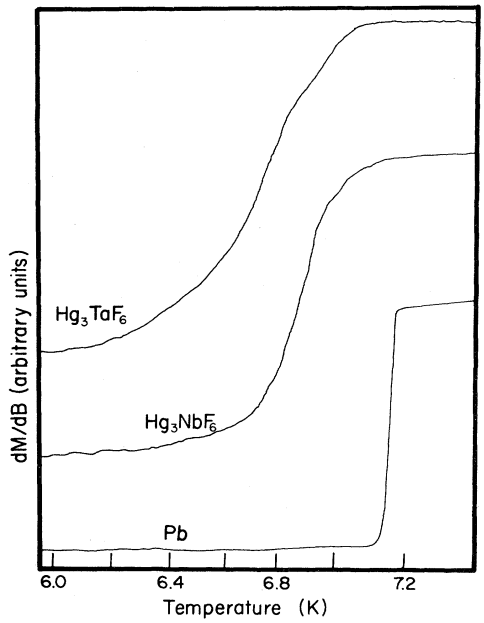

FIG. 1. ac susceptibility of microcrystalline Pb, Hg_3NbF_6, and Hg_3TaF_6 as a function of temperature. Scale of susceptibility is different for each curve.

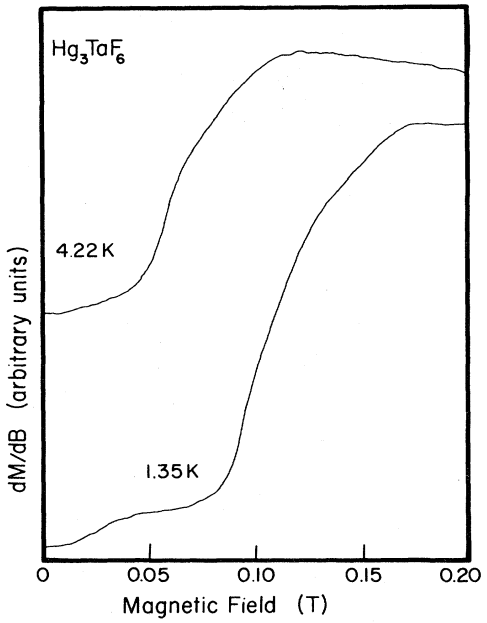

FIG. 3. Transition in Hg_3TaF_6 with changing magnetic field at 1.35 and 4.22 K.

The transition in Hg_3TaF_6 with changing magnetic field is shown in Fig. 3 for two temperatures. The critical field B_c taken at 90% completion during increasing field is 0.087 T at 4.22 K and 0.16 T at 1.35 K. The transitions occur over a magnetic field range of 0.05 T. The transition for Hg_3NbF_6 in Fig. 4 has a critical field of 0.066 T at 4.22 K and 0.12 T at 1.35 K, and occurs over a field range of 0.025 T. Thus, the width of the transition both as a function of temperature and magnetic field is twice as large in Hg_3TaF_6 as in Hg_3NbF_6. This difference may be due to differences in sample quality.

A superconducting transition is evident in Hg_3NbF_6 at 0.038 T at 1.35 K in Fig. 4. The critical-field-temperature relationship between 4.0 and 1.35 K follows that for mercury and the transition is attributed to unreacted mercury in the compound. The change in the differential magnetization from the mercury transition compared to that of Hg_3NbF_6 was 1.2 for the sample of small crystals and 0.2 in the single platelet. The superconducting properties of the compound are independent of the amount of mercury in it. Finally, it should be noted that there was no unreacted mercury that could be detected in Hg_3TaF_6.

Plots of the critical field versus temperature for both compounds are given in Figs. 5 and 6. Both extrapolate to the critical temperature $T_c=7.0$ K at zero magnetic field. The critical field B_0 at $T=0$ K is estimated by assuming that the critical-field-temperature relationship is parabolic below 2 K and making a linear extrapolation of B_c vs T^2. This analysis yields $B_0=0.13$ T for Hg_3NbF_6 and $B_0=0.17$ T for Hg_3TaF_6. These parameters are used in plots of

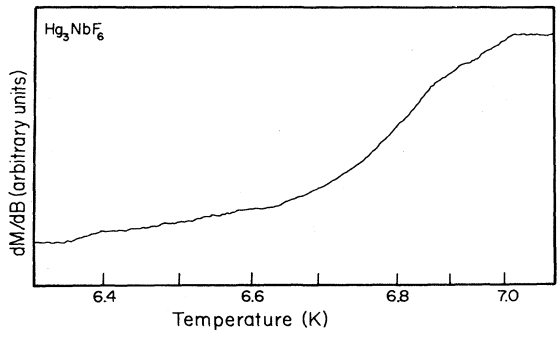

FIG. 2. Temperature dependence of the ac susceptibility of a single-platelet of Hg_3NbF_6 between 6.2 and 7.2 K.

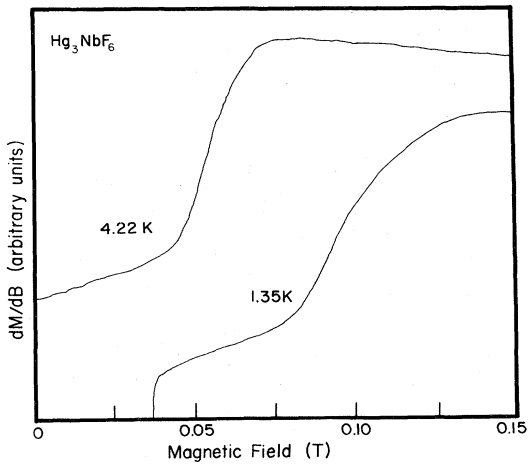

FIG. 4. Transition in Hg_3NbF_6 with changing magnetic field at 1.35 and 4.22 K.

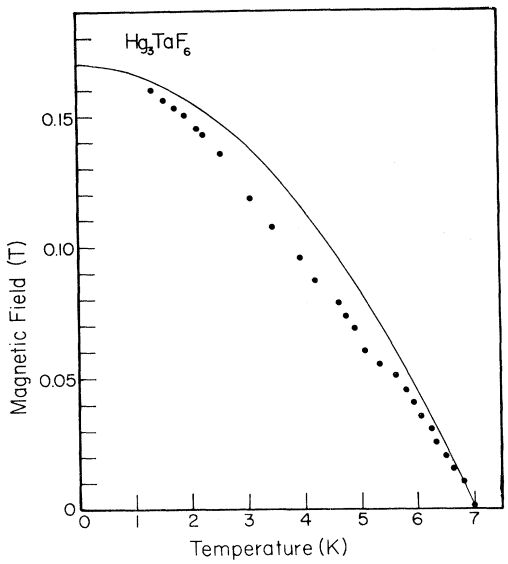

FIG. 5. Critical field vs temperature for a sample of small crystals of Hg_3TaF_6. Curve is calculated from Eq. (1) with $B_0=0.134$ T and $T_c=7.0$ K.

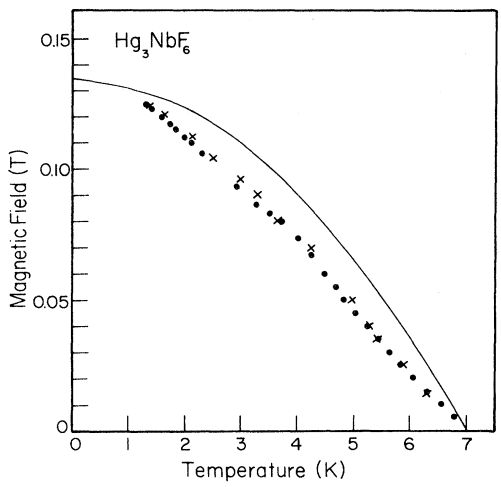

FIG. 6. Critical field vs temperature for Hg_3NbF_6. Closed circles are for a sample of small crystals and the X's are for a single platelet. Curve is calculated from Eq. (1) with $B_0=0.17$ T and $T_c=7.0$ K.

$$B_c=B_0\left[1-\left[\frac{T}{T_c}\right]^2\right] \tag{1}$$

in Figs. 5 and 6. This relationship is not followed particularly closely by either compound. Deviations from the predictions of Eq. (1) are the same for both compounds within experimental error. Also plots of B_c/B_0 vs T/T_c are identical within experimental error so that the change of critical field with temperature is very similar for the two compounds.

The critical field for the single platelet of Hg_3NbF_6 at temperatures down to 1.35 K is the same with the magnetic field parallel and perpendicular to the c axis and shows no directional dependence. It is also independent of the direction of the modulation field in the crystal. Thus, no anisotropy was observed although it should have been detected if it existed since the c axis of the crystals in the platelet are perpendicular to the surface of the platelet. Also, a difference between the critical fields of the platelet and the sample containing small crystals would exist if there is anisotropy in the critical magnetic field. However, there is excellent agreement of the data of the two samples as seen in Fig. 6, again indicating no anisotropy of the critical magnetic field.

IV. DISCUSSION

A comparison of the superconductivity of Hg_3NbF_6 and Hg_3TaF_6 shows that the critical temperature of both compounds is the same to within 1%. The temperature dependence of the critical field is very similar and shows similar deviations from Eq. (1). There is a difference of approximately 20% in the measured critical fields for the two compounds, but this is not especially significant because the measured critical field depends on sample shape and size which have not been taken into account. Thus the superconducting properties of these isostructural compounds are very similar. The superconductivity may be due to the mercury layers which have the same structure in both compounds. However, if the superconductivity were limited to the mercury layers which are separated by 7.68 Å, anisotropy of the critical field and a difference between the data of the polycrystalline sample and the flat platelet would be expected. This anisotropy is not observed which implies that the superconductivity is three dimensional.

The present results contrast with superconducting effects of the linear-chain mercury compound $Hg_{3-\delta}AsF_6$. This superconductivity, which was at first observed[2,3] to be one dimensional, is attributed to mercury dispersed in isolated regions throughout the sample[4] and to mercury trapped within the sample.[5] The superconductivity of the mercury compounds reported here is different from and independent of that of mercury. Secondly, the ac susceptibility of the linear-chain mercury compound changes quickly with magnetic field near zero field and is anisotropic below the critical temperature of mercury. This effect is not present in Hg_3TaF_6 in which there is no mercury and in Hg_3NbF_6 in which there is mercury. The ac susceptibility of the compounds follows that expected for superconductors following the Meissner effect. Future experiments with these compounds require large single crystals obtained from improved crystal-growing techniques which must be developed. This would allow a further search for anisotropy in the critical magnetic field and measurement of resistivity.

V. CONCLUSIONS

Hg_3TaF_6 and Hg_3NbF_6 are superconductors with a critical temperature of 7.0 K. The temperature dependence of the critical field is similar for the two compounds. The critical field extrapolated to $T=0$ K is 0.17 T for Hg_3TaF_6 and 0.13 T for Hg_3NbF_6.

ACKNOWLEDGMENT

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