energy, i.e., near T_c. In the present experiments the fluctuation energy was made comparable with the coupling energy well below T_c by introducing external noise. A comparison of the present results with the earlier ones shows considerable similarity in the effects in the junction I-V characteristics.

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SUPERCONDUCTIVITY OF HYDRIDES AND DEUTERIDES OF THORIUM*

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Superconductivity has been observed in the hydrides and deuterides of thorium with H- or D-to-metal atom ratios of 3.6 to 3.65. Transition temperatures fall in the range from 8.05 to 8.35 K. These materials are apparently type-II superconductors with H_{c2} of the order of 25-30 kG at 1.1 K. There is no evidence for an isotope effect within the limits of experimental uncertainty.

Hydrides with H-to-metal atom ratios of 2 or greater are found among the transition elements, the rare earths, and the actinides. Most of these exhibit metallic electrical conduction and there is evidence[1] that the proton of the hydrogen atom goes into the lattice giving up its electron to the conduction band. The hydrogen in these systems is thus in high concentration and in the metallic state and so the hydrides may be thought of as alloys or intermetallic compounds of metallic hydrogen and the host metal.

There has been theoretical speculation[2] that metallic hydrogen might be a high-temperature superconductor, in part because of the very high Debye frequency of the proton lattice. With high concentrations of hydrogen in the metal hydrides one would expect lattice modes of high frequency and if there exists an attractive pairing interaction one might expect to find high-temperature superconductivity in these systems also.

Superconductivity has been sought in a number of metal hydrides of high hydrogen concentration without success, according to the literature. Negative results have been reported on hydrides of Nb,[3] V,[1] Zr,[4] Ti,[4] La,[5] and the dihydride of Th.[4]

We report here evidence that one such system, the higher hydride of thorium, is superconducting.

Earlier work on the Th-H system[6] shows that there are two identifiable hydrides of thorium corresponding to the formulas ThH_2 and Th_4H_{15} (referred to here as the dihydride and higher hydride, respectively). Crystal structures and lattice constants for these compounds have been determined. Single-phase regions with somewhat uncertain boundaries exist in the phase diagram at about these compositions. The work reported here is primarily concerned with these two single-phase regions; however, samples of mixed phase exhibit properties which appear to be a superposition of the properties of the two phases.

The samples for these studies were prepared in our laboratory from crystal-bar Th reported to be 99.95% pure by the supplier, Alfa Inorganics of Beverly, Mass. Mass spectrographic analysis showed no metallic impurity in concentration greater than 200 ppm.

The hydriding was done in a closed Pyrex system, where the Th reacted directly with pure H_2 or D_2 at elevated temperatures. The composition was determined from the amount of H_2 or D_2 taken up, measured volumetrically. The concentrations reported here are believed to be accurate to about 1%. To prepare the higher hydride, crystalline Th was made to react to the dihydride, powdered in an inert atmosphere, and finally made to react to the concentrations indicated at the lowest temperatures at which the reaction would proceed. The samples ranged in size from 0.2 to 0.5 g and were sealed in thin-walled Pyrex tubes with a partial pressure of He to maintain thermal equilibrium in the low-temperature experiments.

The diamagnetism of the samples was measured using an ac mutual-inductance method. The magnetometer consisted of a primary coil wound coaxially with a balanced secondary pair connected in series opposition, with the sample contained in one of the pair. Ac power at 27 Hz was supplied to the primary from the reference signal of a Princeton Applied Research HR-8 lock-in detector which was also used to measure the output voltage from the secondary. The peak current to the primary was 1 mA, giving a peak measuring field of 0.020 G. The field for the magnetic studies was generated by a small superconducting solenoid. Temperatures above 4.2 K were measured with a calibrated Ge thermometer, the calibration of which was checked to within 0.03 K against the superconducting transitions of Pb and Nb.

The results of magnetic moment measurements on two samples of the higher hydride and two of the higher deuteride are shown in Fig. 1 and the effect on the diamagnetism of one of the samples of hydride are shown in Fig. 2. All four samples shown in Fig. 1 were prepared in the same way, as nearly as we could tell, but variations in homogeneity and particle size could account for the differences among the samples. A Debye-Scherrer x-ray diffraction pattern taken on sample No. 5 showed the complete pattern for Th_4H_{15} and no sign of oxide, Th metal, or the dihydride.

There appears to be no evidence for an isotope effect considering the variation of properties from sample to sample. The variation of the diamagnetic moment with temperature is of the form one would expect if the effective particle size were of the same order as the penetration depth. Values for the critical temperature, obtained by extrapolating the steepest portion of the curve, fall in the range from 8.05 to 8.35 K. At the lowest temperatures, 1.1 K, all four samples appeared to be totally diamagnetic.

The magnetic-field study shows the higher hydride to be a type-II superconductor with a higher

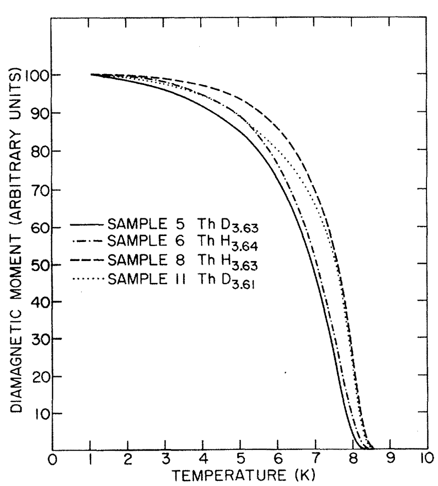

FIG. 1. Temperature dependence of the diamagnetic moment of the higher hydrides and deuterides of thorium.

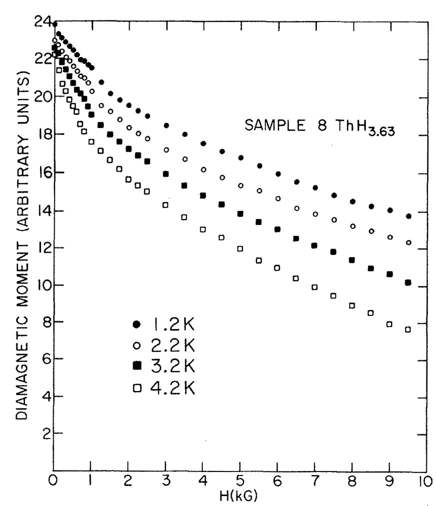

FIG. 2. Effect of a magnetic field on the superconductivity of thorium hydride.

critical field H_{c2}, extrapolated from our measurements, of the order of 25-30 kG.

Measurements on several samples of the dihydride and the dideuteride indicate clearly that these compounds are not superconducting, consistent with an earlier report.[4]

Most of the results presented here have been corroborated by work done at Los Alamos.[7] Their transition temperatures differ by 0.5° to 1° from ours for the higher hydrides and deuterides, probably due to differences in composition.

The apparent absence of an isotope effect is puzzling and deserves more careful study, but on present evidence one would infer that the high-frequency lattice modes simply do not participate in the superconducting interaction.

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EXPERIMENTAL DETERMINATION OF THE PAIR SUSCEPTIBILITY OF A SUPERCONDUCTOR*

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An excess tunneling current due to order-parameter fluctuations has been found in tin-tin oxide–lead junctions just above the transition temperature of tin. Details of the variation of the excess current with voltage, magnetic field, and temperature are in agreement with a calculation by Scalapino in which the excess-current voltage characteristic is a direct measure of the frequency– and wave-number–dependent pair susceptibility characteristic of the superconducting transition. Estimates of the pair relaxation frequency in tin based on the data are 50% greater than theoretical predictions.

In a second-order phase transition, the coupling of the order parameter to an external field may be used to determine the susceptibility associated with the onset of the ordered phase. The susceptibility in turn is a quantity possessing clear theoretical significance which may be compared directly with the results of calculations of the fluctuations associated with the transition. In a recent Letter Scalapino[1] showed that the relevant susceptibility for the superconducting phase transition, the pair susceptibility, could be determined in a simple dc tunneling experiment. Ferrell[2] originally suggested that the pair susceptibility could be obtained by measuring the frequency-dependent conductivity of a Josephson junction. In the experiment proposed by Scalapino, the pair susceptibility of a metal just above its transition temperature is obtained from measurements of an excess current in the dc I-V characteristic of a tunneling junction in which one side of the junction is the metal of interest, near its transition temperature, while the other side is a superconductor well below its transition temperature. In this Letter we report measurements on tin–tin oxide–lead junctions which exhibit an excess current whose behavior is consistent in detail with Scalapino's calculation. The data indicate that dc tunneling measurements are a direct probe of the frequency– and wave-number–dependent pair susceptibility of a superconductor. Earlier studies of electrical conductivity,[3,4] magnetic susceptibility,[5] and quasiparticle tunneling[6] involve convolutions of the pair susceptibility and are thus indirect.