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PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE OF Th_4H_{15}

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Measurements of the superconducting transition temperature of Th_4H_{15} under hydrostatic pressure up to 28 kbar are reported. The initial linear increase is found to be +42 mK/kbar.

RECENTLY there has been some interest in metal–hydrogen systems reaching superconducting transition temperatures of about 8 K in the case of Th_4H_{15}[1] and up to 16 K in the case of the Pd–Ag–H system.[2] In contrast to the Pd–H-system, where the high transition temperature could only be reached by ion implantation at low temperature, Th_4H_{15} is a stable compound at room temperature. Although in both cases the large increase in T_c is caused by hydrogenating Th and Pd, respectively, the situations are quite different: Pd itself is a metal with a high electronic density of states and a highly exchange enhanced magnetic susceptibility and is not superconducting. Th, however, which is found at a quite different place in the periodic system, shows superconductivity at about 1.4 K and has a low density of states.

The increase in T_c in the Pd–H-system has been understood as a consequence of the suppression of spin fluctuations in Pd,[3] but to date the reasons why Th_4H_{15} is a high T_c superconductor are not clear. In order to get further insight into this problem, we have measured the influence of hydrostatic pressure on the superconducting transition.

Our sample has been prepared as described earlier in some detail[4] and its properties may be found there too. We note that Th_4H_{15} of approximately stoichiometric composition has been found to exist in more than one crystalline modification.[5] A cubic phase has been identified corresponding to the published structure[6] which is superconducting and a non-superconducting phase which is a tetragonal distortion of the cubic structure has also been found. In addition, depending upon subtle differences in preparation, transition temperatures falling in two ranges, 7.5–8.0 and 8.5–9.0 are found and these two modifications are not distinguishable by X-ray diffraction. The bulk sample used in the pressure experiments reported here appears to be totally of the lower T_c cubic modification. Its volume is about 2 mm^3 and the shape is the same as the original thorium metal, but expanded by about 11 per cent

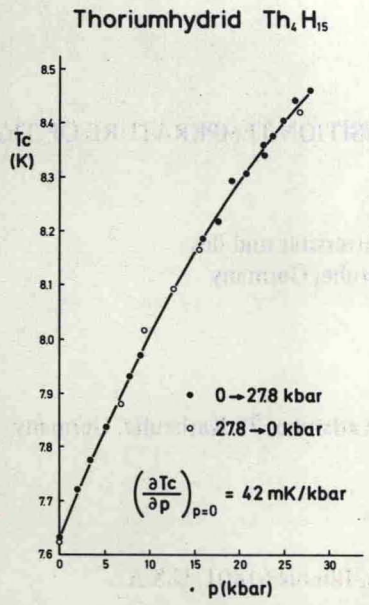

FIG. 1. Transition temperature T_c of Th_4H_{15} vs hydrostatic pressure p. The transition width is about 0.3 K and remains fairly constant.

in all directions. The transition temperature is 7.6 K.

A piston and cylinder arrangement with a fluid pressure medium was used to generate hydrostatic pressure as described in references 7, 8 and 9. Constructive improvements and the materials used for the high pressure environment are found elsewhere.[10] The pressure reached at low temperatures was about 28 kbar. This was determined by the depression of the superconducting transition temperature of tin, using the low temperature compressibility data of reference 11 to obtain the relative volume changes. The pick-up coil, which detected the magnetic susceptibility of the sample, was located within the fluid pressure transmitting medium. The temperature was determined by a Cryocal germanium resistor.

In the Fig. 1 we have plotted the transition temperature T_c against the applied pressure p. The measurements have been performed both with increasing pressure up to 27.8 kbar and with decreasing pressure back to zero, thereby indicating the lack of any irreversible change of the sample. The initial increase is 42 mK/kbar. Although the lack of any compressibility data for Th_4H_{15} prevents a proof, it can be assumed that a plot of T_c vs $\Delta V/V$ would be linear. The increase of T_c does not saturate in the investigated pressure region. It might be argued that under pressure a gradual transformation from the lower to the higher T_c cubic phase would account for the positive dT_c/dp. It is unlikely, however that such a transformation would be as reversible as the results indicate.

One of us (C.B.S.) is presently cooperating with the neutron scattering group at Argonne Laboratory in both elastic and inelastic scattering experiments to determine the phonon density of states and to look for possible structural modifications. These experiments could tell us, whether the T_c's may be explained in terms of electron–phonon interaction or possible mode softening. However, the lack of a significant isotope effect[1] leads one to look for a change in the electronic properties rather than in the phonon properties.

In this sense we offer a possible explanation of the rather large pressure effect in Th_4H_{15}. As has been suggested by Hill,[12] the 5*f*-electrons of the early actinides are often better compared to the 3*d*-electrons of the first transition series than to the 4*f*-electrons of the rare-earth series. Hill's arguments were based on band structure calculations of Kmetko[13] and supported by comparing bandwidths rather than symmetries. Sharing this point of view, we assume that in thorium the addition of hydrogen does not change the 3*d*-transition metal behaviour, but enhances it and accounts for the higher T_c of Th_4H_{15}. Also the bandwidth has decreased by hydrogenating thorium because of the lattice expansion. A narrow band favours magnetic behaviour and spin fluctuations may now reduce T_c which otherwise would be even higher than 8 K. This situation shows some similarities to that one of vanadium, for which one assumes that T_c would be higher than the actual 5.3 K, if magnetic spin fluctuations were absent. In applying pressure, the lattice expansion is reduced, thereby increasing T_c as has also been observed for V.

Our assumptions are supported by the conditions for uranium: According to its higher nuclear charge, U has a smaller *f*-bandwidth. It is still a superconductor but gets magnetic after hydrogenating to UH_3.[14] We think this is caused at least partly by lattice expansion and band narrowing. One may