Superconductivity of molybdenum hydride and deuteride

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Superconductivity has already been observed in bulk samples of hydrides of two d elements, which are palladium[1] and titanium,[2] whereas palladium–hydrogen[3] and titanium–hydrogen[4] systems exhibit an "inverse" isotopic effect: for the same hydrogen–metal ratio n the superconducting titanium temperature T_c is higher for the deuteride than for the hydride.

We shall report observations of superconductivity in a hydride and a deuteride of another d element, this time molybdenum.

Samples of molybdenum were cut by spark machining from a single crystal characterized by the resistance ratio $R_{300}K/R_{4.2}K \approx 1000$; this was followed by grinding off a damaged layer of thickness ≈0.05 mm and removal of an additional layer of thickness ≈ 0.03 mm by electropolishing in H_2SO_4. The final dimensions of the samples were ≈ 3×3×0.2 mm. Saturation of the samples with hydrogen involved exposure to an atmosphere of molecular protium (deuterium) at 325°C at a pressure of 60 kbar for 24 h, followed by "quenching" to ≈ −120°C under pressure; the method and conditions during synthesis of molybdenum hydride were described earlier.[5]

Significant evolution of hydrogen from molybdenum hydride and deuteride samples began at atmospheric pressure $T \gtrsim 220$ K. The apparatus used made it possible to study samples without heating at temperatures above 100-120 K; in the intervals between measurements the samples were stored in liquid nitrogen. The values of T_c were determined by the inductive method using the position of the midpoint of a step in the temperature dependence of the magnetic susceptibility χ by pumping out He^3 vapor at temperatures $T \gtrsim 0.3$ K. The critical field H_c was estimated from the position of the step of the $\chi(H)$ isotherms in fields H up to ≈ 280 G. An x-ray diffraction investigation was carried out at 100 K by a photon-counting method using a DRON-2.0 diffractometer and CuK_α radiation. The hydrogen content in the samples was deduced from the amount of hydrogen evolved during thermal decomposition at temperatures up to 500°C by a method described in Ref. 6.

We synthesized and investigated four hydride samples and two samples of molybdenum deuteride. Within the limits of the experimental error, the measured parameters of all four hydride samples were the same and this was also true of two deuteride samples; the average values of the parameters and the properties of the original molybdenum single crystal are listed in Table I.

The results of measureents on molybdenum were in agreement with the published data.[7] Moreover, the values of n and of the parameters of the hcp sublattice of the metal in molybdenum hydride agreed with those published earlier.[5] It is clear from Table I that, within the limits of the experimental error, these values were the same for molybdenum deuteride (not investigated before) and hydride.

The dependences $\chi(T)$ obtained for samples in the absence of a magnetic field are plotted in Fig. 1, whereas the dependences $H_c(T)$ are given in Fig. 2; we can see that the dependences $H_c(T)$ are described satisfactorily by the familiar expression $H_c(T) = H_c(0)\,[1-(T/T_c)^2]$; the values of $H_c(0)$ at T = 0 K and of $dH_c/dT|_{T_c}$ listed in Table I were obtained by extrapolation on the basis of this expression.

The width of the superconducting transition (≈ 0.07 K, Fig. 1) of molybdenum hydride and deuteride was slightly greater than the width of the transition in a molybdenum single crystal and the value of T_c for the hydride was the same as that for molybdenum, whereas that for the deuteride was ≈ 0.2 K higher. The value of $H_c(0)$ for the deuteride was approximately three times that of the hydride and was over six times greater than the value of $H_c(0)$ for molybdenum. After removal of hydrogen from the Mo–H and Mo–D samples by vacuum annealing at 500°C for 30 min the superconducting transition temperature T_c became 0.92 K, i.e., it did not differ from T_c for the original molybdenum, whereas the value of $H_c(0)$ decreased to ≈ 120 G.

TABLE I. Average values of parameters of investigated crystals and of the original single crystal

Sample	n	T_c, K	H_c (0), G	$dH_c dT\|_{T_c}$, G/K
Mo	0	0.92 ± 0.005	≈90	≈200
Mo—H	1.27 ± 0.03	0.92 ± 0.005	≈600	≈1300
Mo—D	1.26 ± 0.03	1.11 ± 0.005	≈300	≈550

Sample	Metal lattice	a, Å	c, Å	c/a
Mo	bcc	3.144 ± 0.003	—	—
Mo—H	hcp	2.932 ± 0.003	4.747 ± 0.003	1.619 ± 0.002
Mo—D	hcp	2.931 ± 0.003	4.747 ± 0.004	1.618 ± 0.002

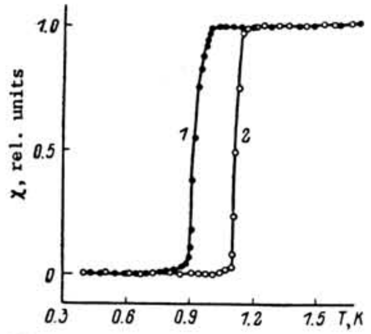

FIG. 1. Temperature dependences of the magnetic susceptibility in the vicinity of the superconducting transition: 1) $MoH_{1.27}$; 2) $MoD_{1.26}$.

Some increase in $H_c(0)$ for molybdenum (from ≈ 90 to ≈ 120 G) as a result of introduction and removal of hydrogen could be due to the lattice defects and residual stresses created by this procedure: an x-ray diffraction investigation demonstrated that the procedure in question converted single crystals into polycrystalline samples with fairly wide diffraction lines.

We thus found a third d element, after Pd (Refs. 1 and 3) and Ti (Refs. 2 and 4), in which the hydride and deuteride are superconducting and – as in the case of Pd and Ti – the value of T_c for the deuteride was higher than for the hydride. An explanation of such an "inverse" isotopic effect in the palladium–hydrogen system, first proposed in Ref. 8 and then confirmed by several theoretical and experimental investigations,[3,7] postulates that palladium hydrides (deuterides) are superconductors of a new type for which a significant contribution to the electron–phonon interaction constant is made by the interaction of electrons with optical vibrations of hydrogen atoms and the higher value of T_c for the deuterides is due to a weaker anharmonicity of the vibrations of the deuterium atoms than that in the case of protium atoms. Clearly, the superconducting phases in the titanium–hydrogen and molybdenum–hydrogen systems also belong to this new class of superconductors.

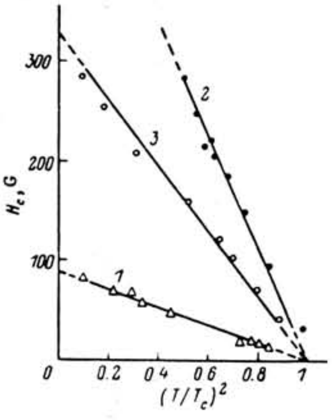

FIG. 2. Dependences of the critical magnetic field H_c on the square of the reduced temperature: 1) Mo; 2) $MoH_{1.27}$; 3) $MoD_{1.26}$.

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