Transfer of hydrogen to octahedral lattice positions in the superconducting titanium hydride phase

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The use of inelastic neutron-scattering method has revealed that hydrogen in a metastable superconducting ϵ phase of $TiH_{0.71}$ occupies principally the octahedral (O) interstitial positions in the metal lattice. In the δ phase of this hydride the hydrogen is found in the tetrahedral (T) positions.

The appearance of or a marked increase in the temperature (T_c) at which pure metals undergo a transition to the superconducting state upon hydrogenation has until recently been observed only in the Pd–H system, in Th_4H_{15} (see Ref. 1), and in the metastable films of TiH_x, ZrH_x, and HfH_x α phases[2] which were obtained by hydrogen implantation at a low temperature. The phonon spectrum of these superconducting hydrides has been studied comprehensively only for PdH_x. For Ti and Zr hydrides the inelastic neutron scattering spectra were studied in equilibrium α phases which do not undergo a transition to the superconducting state.[2,3]

A metastable TiH_x ϵ phase, which is a superconductor with $T_c = 4.2$ K at $x = 0.71$ and $T_c = 2.6$ K at $x = 0.85$, was synthesized by Ponyatovskiĭ *et al.*[4] by quenching under pressure. Upon warming to 110 K the ϵ phase with an orthorhombic structure transforms to an fct δ phase[5] which undergoes a transition to the superconducting phase at $T = 2$ K. We know that the critical temperature of Ti is $T_c = 0.4$ K (Ref. 6).

On the basis of an x-ray-diffraction study Degtyareva *et al.*[5] established that a transformation of the ϵ phase of $TiH_{0.71}$ into a δ phase is accompanied by an appreciable increase of the atomic volume. This circumstance led them to assume that the positions of the hydrogen atoms in the metal sublattice can change (O→T) as a result of a phase transition $\epsilon \rightarrow \delta$.

We report here the results of measurements of the spectra of inelastic neutron scattering in ϵ and δ phases of titanium hydride $TiH_{0.71}$. The sample consisted of forty pellets each 6.7 mm in diameter and 1 mm thick. The sample weight was 6.4 g and the transmission of neutrons with a 1.08-Å wavelength was ~72%. The ϵ phase was obtained by compressing the sample to a pressure $P \cong 60$ kbar, heating it to $T = 620$ K, quenching it to liquid-nitrogen temperature in a time of ~20 s, and bringing the sample down to atmospheric pressure. All the intermediate procedures involving the ϵ-phase sample and its storage were carried out in liquid nitrogen. The δ phase was obtained by heating the sample to $T \cong 310$ K.

The experiments on inelastic neutron scattering were carried out in the IBR-2 reactor at the Joint Institute for Nuclear Research, Dubna. We used a KDSOG-M

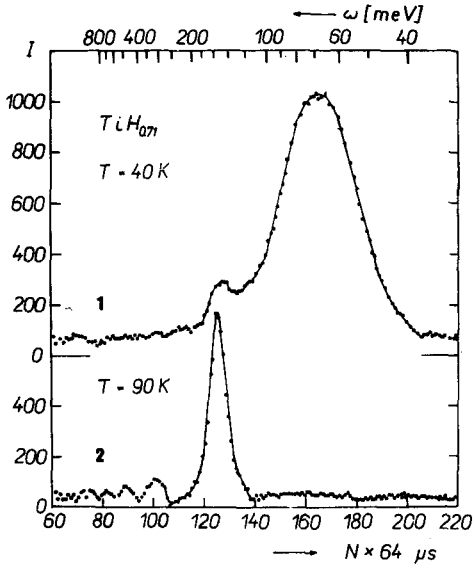

FIG. 1. Inelastic neutron-scattering spectra of the ϵ and δ phases of $TiH_{0.71}$ (curves 1 and 2, respectively).

inverse-geometry spectrometer[7] at temperatures of 40 K (the ϵ phase) and 90 K (the δ phase). The neutron scattering angles were 70°, 90°, 110°, and 130° for the reflection measurements. The spectra for various angles were summed after subtracting the background. The results which we obtained (see Fig. 1) were normalized to a single measurement time. The energy of the detected neutrons was 4.9 meV and the energy transfer was in the range 20–500 meV. To monitor the single-phase composition of the test samples together with the inelastic neutron scattering, we measured the diffraction of neutrons at 30°, 50°, 70°, and 90° angles.

Figure 2 is a plot of the weighted vibrational state density functions[8] $G_H(\omega)$ for the phases under study. The positions and half-widths of the principal peaks (in meV) for the ϵ phase are: $\omega_1 = 75 \pm 2.5$, $\Delta_1 = 44 \pm 4$; $\omega_2 = 156 \pm 3$, $\Delta_2 = 45 \pm 13$;

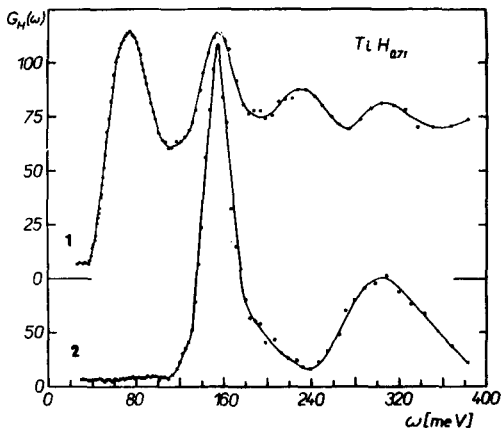

FIG. 2. Generalized frequency distribution function $G_H(\omega)$ for the ϵ and δ phases of $TiH_{0.71}$ in the region of optical oscillations (curves 1 and 2, respectively).

$\omega_3 = 229 \pm 5$, $\Delta_3 = 49 \pm 15$ and for the δ phase: $\omega_1 = 154.5 \pm 1$, $\Delta_1 = 27 \pm 1$; $\omega_2 = 309.5 \pm 2$, $\Delta_2 = 87 \pm 2$; $\omega_3 = 464.5 \pm 5$, $\Delta_3 = 91 \pm 5$.

The ω_1 peak in the ϵ phase stems from the vibration of hydrogen in the O positions of the metal lattice. Analysis of the half-width and intensity of the ω_2 peak shows that the vibration of hydrogen atoms in the T positions may contribute to this peak to some extent. At the same time, the half-width of Δ_1 is much greater than the instrumental resolution, indicating that the vibration of hydrogen in the O positions has a strong dispersion. The effect of the lattice distortion on the width of this peak should also be taken into account.

In the δ phase the observable peaks are caused by the vibration of hydrogen in the T positions (the first, second, and third harmonics, respectively). The condition for a harmonic approximation, $\omega_1 = \omega_2/2 = \omega_3/3$, is satisfied for this phase. The position of the ω_2 peak for the ϵ phase is the same as the position of the ω_1 peak for the δ phase within error limits; i.e., the Ti–H distances in the T positions for these phases apparently are approximately the same.

The frequency of the optical phonons in the δ phase was found to be slightly higher than the vibration frequencies of hydrogen in the T positions of the TiH_x γ phases ($x = 1.3 - 2.0$), which, according to the data of different authors (see Ref. 1), lie in the ranges $\omega_1 = 129$–149 meV and $\omega_2 = 280$–283 meV.

We have thus established that in the metastable superconducting ϵ phase of the Ti–H system, hydrogen occupies principally the O positions and in the nonsuperconducting δ phase it occupies only the T positions. After the V–H system,[1] the Ti–H system is the second system in which hydrogen can occupy both the T and the O positions, depending on the phase state.

With respect to the correlation of the dynamic and superconducting properties, the behavior of this system near the ϵ phase is similar to the situation in palladium hydride, where the phonon spectrum also exhibits a low-frequency optical peak with a large dispersion. The superconductivity in Pd–H has been linked[1] with a large contribution of the optical vibrations of hydrogen to the electron-phonon coupling constant λ, whereas in other superconductors the principal contribution to λ comes from the acoustic phonons.

The nature of the superconductivity of the ϵ phase of titanium hydride can be determined by obtaining additional information on the low-frequency part of the phonon spectrum and on the electronic properties.

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