

Tritium vibrations in niobium by neutron spectroscopy

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We report here the first measurement of tritium vibrations in a metal. Neutron spectra for tritium in niobium are compared with results for niobium deuteride and hydride in the same (β) crystal phase to reveal deviations from a \sqrt{M} dependence, reflecting the anharmonicity of the potential. Vibration peaks are also observed for dilute H and O impurities in the niobium sample.

Studies of the vibration spectra of hydrogen isotopes in metals provide information which is essential for the interpretation of the novel phase transformations and thermodynamic and physical properties of metal-hydrogen systems.¹ Extensive neutron scattering measurements of vibrational density of states and dispersion curves have been reported^{2,3} for hydrogen and deuterium in metals. However, no experiments have thus far been reported for tritium-metal systems. Such measurements are both difficult and complex, since the tritium cross section (≈ 1.5 b) is about two orders of magnitude smaller than for H and because they require handling of samples containing hundreds of Ci of tritium activity.

In this Communication, we describe the results of the first measurement of the vibration spectrum of tritium in a metal (niobium) and directly compare the vibration frequencies of NbT_{0.2} with optical vibration peaks measured under identical experimental conditions for NbD_{0.72} and NbH_{0.32}.⁴ In all three samples, the bulk of the hydrogen isotope present is in regions of β -phase material.

A 50-mm-high bundle of 0.4-mm niobium wires weighing 10.45 g was loaded at 300 °C with tritium to an average concentration⁵ of NbT_{0.2} (687 Ci of tritium) at the General Electric Company's Neutron Devices Department. The sample was then mounted in the center of a 20-mm-diam, 100-mm-high molybdenum cylinder, with the walls machined down to 0.5 mm in the area of the sample to minimize background. Measurements of neutron spectra were made at the NBS reactor using the BT-4 triple-axis spectrometer with a Cu(220) monochromator (40' collimation before and after the monochromator) and a new low-background Be-filter analyzer with a 230-cm² detector set at an angle of 80° to the incident beam. Neutron energies were varied continuously to

allow spectra to be measured from 40 to 200 meV energy transfers. The energy resolution varied from 5 to 6% between 40- and 100-meV energy transfer and from 5.5 to 6% between 100 and 200 meV.

The neutron spectrum of NbT_{0.2} is shown in Fig. 1, along with the results for NbD_{0.72} and NbH_{0.32}. At these concentrations, all samples should be at least 85% β phase so that effects on the spectra of the residual α (solute) phases will be small. The NbT_{0.2} spectrum was corrected for background by subtracting an identically measured "blank" spectrum obtained from a 10.5-g bundle of Nb wires surrounded by a thin Mo sheet. The deuteride and hydride spectra are corrected only for fast neutron background from the sample measured with cadmium covering the analyzer cavity.

The results for NbT_{0.2} show two dominant peaks at 72 ± 1 and 101 ± 1 meV, due to optical vibrations of tritium in the slightly distorted tetrahedral sites in the quasicubic (orthorhombic) β -phase structure. An isolated atom bound in a tetrahedral site of a bcc lattice would have two optical vibrational modes, the higher-energy mode being doubly degenerate. The ratio of integrated intensities of the high- and low-energy peaks (about 2 to 1) is consistent with such a prediction. The widths of the observed density-of-states peaks, corrected for resolution, are about 5 and 10 meV, respectively, and are presumably due primarily to phonon dispersion due to T-T interactions in the β -phase structure, although the small (~ 15 at. %) amount of tritium in the α phase would also tend to broaden these peaks.

It is interesting to note the presence of two weaker peaks in the NbT_{0.2} spectrum. The peak energy of 121 ± 2 meV is assigned to ~ 0.1 at. % H in the sample (measured by mass spectroscopic analysis to be ~ 0.5 at. % of the hydrogen isotopes present). The

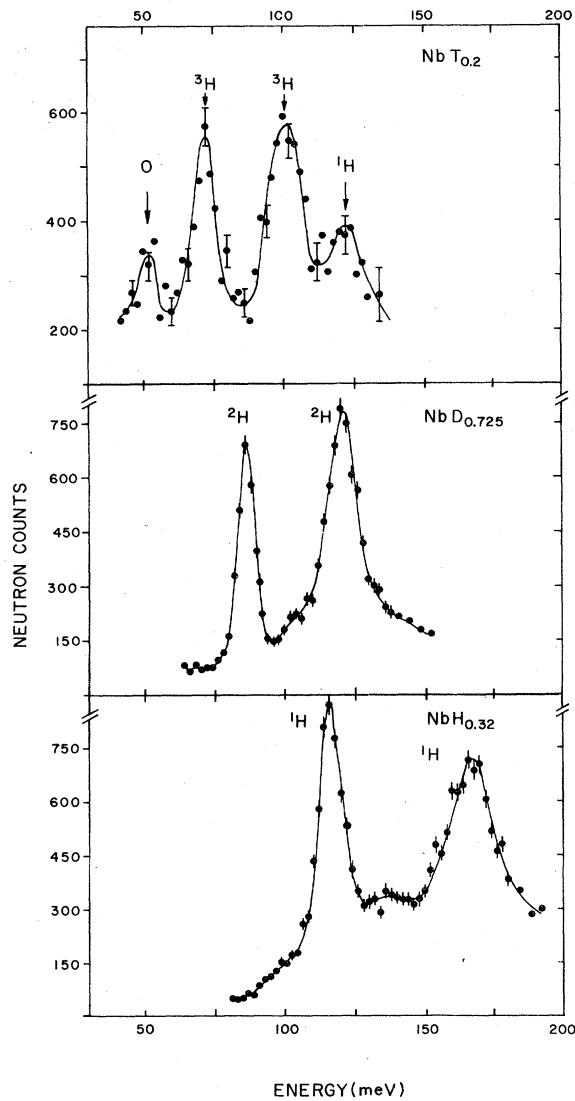


FIG. 1. Neutron spectra for $\text{NbT}_{0.2}$, $\text{NbD}_{0.725}$, and $\text{NbH}_{0.32}$ at 295 K. Assignments of various vibration peaks for different isotopes are indicated.

vibration peak for these protons surrounded by unlike tritium oscillators is apparently shifted significantly from the value of 116 meV for hydrogen bound in an isotopically pure β phase at 295 K [see Fig. 1(c) and Table I]. The second subsidiary peak at 52 meV is apparently due to the vibrations of ~ 1 at. % oxygen impurities diffused into the sample during the high-temperature loading. The blank sample showed a weaker peak at the same energy which could be associated with a small amount of O present in the Nb sample before loading. The comparable intensities observed for the H and O impurity peaks are consistent with the fact that the O neutron cross section is an order of magnitude lower than for H.

The comparable neutron spectra measured for niobium deuteride and hydride are also shown in Fig. 1, and the peak vibration frequencies for all the isotopes are listed in Table I, along with the comparison of the observed frequencies for the two vibration peaks (ω_1 and ω_2) with that predicted for a purely harmonic potential. As can be seen from Table I, both H and D vibrations exhibit an isotope shift with respect to T significantly less than that expected for a harmonic potential. Moreover, the results show that the deviation for $\text{NbH}_{0.72}$ with respect to the tritium frequencies is greater than that for the deuteride. These and other recent results for β -phase niobium hydrides^{4,6} are generally consistent with isotope shifts for the first excited levels predicted on the basis of a model assuming small anharmonic disturbances to a parabolic potential.⁴ We attempted in our experiments to measure the second harmonic of the 72-meV peak in the tritide but were unable to observe a clearly distinguishable peak, as recently observed for β -phase niobium^{4,6} and tantalum⁶ deuterides.

Neutron measurements are planned on the α phase of tritium in Ta and on the β phase of vanadium tritide, including a further search for second harmonics.

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TABLE I. Peak frequencies observed for ^3H , ^2H , and ^1H bound in β -phase niobium hydride. Ratios of the frequencies for different isotopes to those predicted for a harmonic oscillator are shown normalized to the tritide frequencies. M_T and M represent the masses of tritium and the lighter isotopes, respectively.

	$\hbar\omega_1$ (meV)	$\hbar\omega_2$ (meV)	$\frac{\omega_1(M)}{\omega_1(T)} \left(\frac{M}{M_T}\right)^{1/2}$	$\frac{\omega_2(M)}{\omega_2(T)} \left(\frac{M}{M_T}\right)^{1/2}$
^3H	72 ± 1	101 ± 1	1	1
^2H	86 ± 1	120 ± 1.5	0.975 ± 0.018	0.970 ± 0.016
^1H	116 ± 0.7	167 ± 1.5	0.930 ± 0.014	0.955 ± 0.013

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¹For a general review, see *Hydrogen in Metals I and II*, Topics in Applied Physics, edited by G. Alefeld, and J. Völkl (Springer-Verlag, New York, 1978), Vols. 28 and 29.

²T. Springer, Ref. 1, Vol. 1, pp. 75–98.

³J. M. Rowe and J. J. Rush, *Neutron Inelastic Scattering* (IAEA, Vienna, 1978), Vol. II, p. 303.

⁴Similar β -phase measurements for $\text{NbH(D)}_{0.8}$ have recently

been reported [D. Richter and S. M. Shapiro, Phys. Rev. B 22, 599 (1980)]. The present results are in good agreement with these data.

⁵D. R. Begeal, Report No. SC-DR-710789 (unpublished).

⁶J. J. Rush, A. Magerl, and J. M. Rowe (unpublished); for preliminary report see Bull. Am. Phys. Soc. 26, 337 (1981).