Observation of low-energy excitations in NbD: A simple lattice-dynamical model

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A tentative explanation of the 18–19 meV peaks recently observed in $NbD_{0.85}$ is presented. These peaks are attributed to the presence of flat optical modes in the lattice dynamics of β-phase NbD. These modes have significant structure factors over the whole pseudocubic zone in a multidomain crystal, mainly as a result of a large deuterium amplitude. Similar peaks in the α' phase of $NbD_{0.85}$ can also be explained as a "resonant interaction" where the broadening is due to the increased disorder.

INTRODUCTION

There has been great interest in the lattice dynamics of metals containing hydrogen in recent years.[1] In particular, previous measurements[2,3] on $NbD_{0.85}$ have revealed the existence of a "branch" at 18–19 meV in both the β phase and the α' phase,[4] which has not been observed in earlier measurements[5-7] on NbD_x. In an experiment on low-concentration $NbH_{0.05}$, a peak has been observed[8] near that energy. This peak was explained as a resonant enhancement of the hydrogen vibration amplitude for a particular set of host-lattice acoustic modes. The theory used in this case applies only to the low-concentration problem, and so a different method is required for the high-concentration alloys.

We have calculated the lattice dynamics and one phonon-neutron scattering structure factor of β-phase NbD using a Born–von Kármán model with interactions extending to the third-nearest metal neighbors and with nearest-neighbor metal-hydrogen interactions. Although most of the calculations were done for stoichiometric NbD, some attempts were made to simulate the effects of vacancies by using a cell containing two primitive β-phase NbD cells, a smaller version of the procedures used earlier for PdH_x (Ref. 9) and PdD_x (Ref. 10).

THE MODEL

The structure of NbD_x with concentrations x close to equiatomic was first studied by Somenkov *et al.*[11] For the β phase, an orthorhombic structure with space group P_{nnn} with Nb in f sites (000, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$) and deuterium (D) in a sites ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$) and in b sites ($\frac{3}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$) was given. However, the correct space group of β-phase NbD is C_{ccm} with Nb in e sites ($\frac{1}{4}\frac{1}{4}0$, $\frac{1}{4}\frac{3}{4}\frac{1}{2}$) and D in a sites ($00\frac{1}{4}$, $00\frac{3}{4}$). Although this unit cell has a volume of a^3 (a = length of the cubic axis), the space group P_{nnn} with a volume of $2a^3$, as originally given by Somenkov *et al.*, was used to calculate the lattice dynamics of β-phase NbD_x. Leaving out one D atom from this unit cell can be looked upon as a simple model for a β-phase NbD_x crystal with a high concentration of defects (although they are ordered in this model) such as was used in the measurements by Shapiro *et al.*[2]

The model does not take into account small distortions in metal atom arrangement with respect to the cubic symmetry such as have been measured by Pick and Bausch.[12] The orthorhombic character is introduced only by the fact that the D occupies $\frac{1}{6}$ of the tetrahedral interstitial sites on a particular sublattice.

Within this framework there are three possible orthorhombic cells according to the D ordering in chains along the [110], [101], or [011] direction (all notations are given for the cubic unit cell of the host lattice). The multidomain feature of the sample used to date has been taken into account by assuming equal volumes of these three different orthorhombic domains.

A three-neighbor Born–von Kármán model was used to describe the Nb-Nb interactions. As might be expected from the complicated dispersion relations of Nb, such a model gives a poor description of the details of the dispersion curves. However, since the main goal of this investigation was to study the influence of the orthorhombic structure and of the multidomain character of real crystals on measurements of the phonon dispersion relation of β-phase NbD_x, this model should suffice.

The Nb-Nb force constants were taken from a fit of six acoustic-phonon branches in $NbD_{0.45}$ (Ref. 5). By choosing $NbD_{0.45}$ rather than Nb, one can partly take into account the general tendency of the phonon frequencies of the host metal to

TABLE I. The first line shows the force constants (10^3dyn/cm) for a 3-neighbor Born–von Kármán fit to the phonon modes of $NbD_{0.45}$ (Ref. 4) and the Nb-D force constant. The force constants in line 2 were used to calculate the phonon relation in Fig. 1. The force constants shown in lines 3 and 4 give similar results as the ones shown in Fig. 1.

1st neighbor		2nd neighbor		3rd neighbor			Nb-D
ϕ_{xx}^{111}	ϕ_{xy}^{111}	ϕ_{xx}^{200}	ϕ_{yy}^{200}	ϕ_{xx}^{220}	ϕ_{zz}^{220}	ϕ_{xy}^{220}	ϕ
15.5	11.5	12.9	−0.9	−7.1	2.0	0.6	14.0
15.5	11.5	12.9	−0.9	7.0	2.0	0.6	14.0
15.5	11.5	42.0	−0.9	−7.1	2.0	0.6	14.0
15.5	−3.0	12.9	−0.9	−7.1	2.0	0.6	14.0

increase upon hydrogen alloying. This set of force constants is given in line 1 of Table I.

Central forces[13] were used to describe the interaction of the D with the four nearest-neighbor Nb. The first derivative of the potential was set equal to zero to assure equilibrium. The force constant was then adjusted to 14 000 dyn/cm to give the high-energy vibrations of the D at 85 meV and at 120 meV. (The dispersion of these high-energy branches as calculated by this model is of the order of 3 meV.)

The phonon energies $\nu(\vec{Q},i)$ (meV) and the "normalized" structure factors $g(\vec{Q},i)$ (relative units) were calculated for the same phonon branches as shown in Ref. 2. The structure factors were calculated for 300 K according to the following equation:

$$g(\vec{Q},i)=\frac{n_i+1}{\nu_i Q^2}\left|\sum_{k=1}^{3N}\frac{b_k}{\sqrt{m_k}}\vec{Q}\cdot\vec{e}(k,\vec{Q},i)\right|^2. \quad (1)$$

b_k and m_k are the coherent scattering lengths ($b_{Nb}=7.1$, $b_D=6.7$ in fm) and the masses ($m_{Nb}=93$, $m_D=2$ in amu). The summation index k includes all N particles in the unit cell as chosen above. n_i is the phonon occupation number for a phonon of energy ν_i, and n_i+1 corresponds to a scattering geometry where a phonon is created. $\vec{Q}$ is the total wave-vector transfer of the neutron. Notice that the structure factor as calculated in Eq. (1) is normalized for $|Q|=1$.

The phonon branches, as calculated in the orthorhombic structures, were mapped back into the Brillouin zone of the bcc Nb lattice in order to allow the results to be compared easily with the data in Refs. 2 and 3.

RESULTS

The calculations from this model revealed low-frequency branches with strong structure factors at 10 meV and another flat branch with considerably smaller structure factors at 20 meV. In order to improve the agreement with the experiments, the Nb-Nb force constants were adjusted one by one to increase the frequency of the lower branch so that the two flat branches were nearly degenerate at the zone center with an energy of about 20 meV. This could be achieved by changing ϕ_{xy}^{111}, ϕ_{xx}^{200}, or ϕ_{xx}^{220} to the values given in lines 2 through 4 in Table I. The other force constants had little influence on these flat branches.

The result for *one* set of force constants with $\phi_{xx}^{220}=7.0\times10^3$ dyn/cm is shown in Fig. 1. The phonon branches are only shown as long as their structure factor is reasonably large, a criterion which we arbitrarily took to be 10% of the structure factor for the (100)L phonon mode in pure Nb calculated from the same model leaving out all D.

Similar calculations have also been performed for the other two sets of force constants as given by lines 3 and 4 in Table I. In the following, we want to point out some features which are similar for all three sets of force constants. However, these calculations have shown that the relative intensities of the various branches are strongly force-constant dependent. Therefore, it is not useful to undertake detailed line-shape comparisons with the experimental results. It should be noted that for all sets of force constants given in Table I, the overall shape of the acoustic modes is approximately constant, while the flat optic modes change somewhat.

(I) The salient feature in Fig. 1 is the large number of phonon branches observed. This is due both to the lowered symmetry of β-phase NbD and to the multidomain nature of the crystal. In particular, there are always modes at an energy of about 20 meV, independent of the wave vector and the polarization.

(II) Generally the structure factors of the branches at 20 meV are strong, i.e., comparable to the structure factors of phonons at the same energy in pure Nb, as calculated from a similar model. In some cases, the structure factors for the branches around 20 meV become smaller at the zone boundary than they are at the zone center. Near the (1,1,1) point they are too small to be shown in Fig. 1 using the above criterion. However, introducing defects in the way described earlier, increases the structure factors near that point considerably. It should also be pointed out that these flat branches will contribute to a high phonon density of states at 20 meV. Since about 25% of the total cross section of D is incoherent, there will always be a peak from the density of states at this energy in addition to the coherent phonon peak.

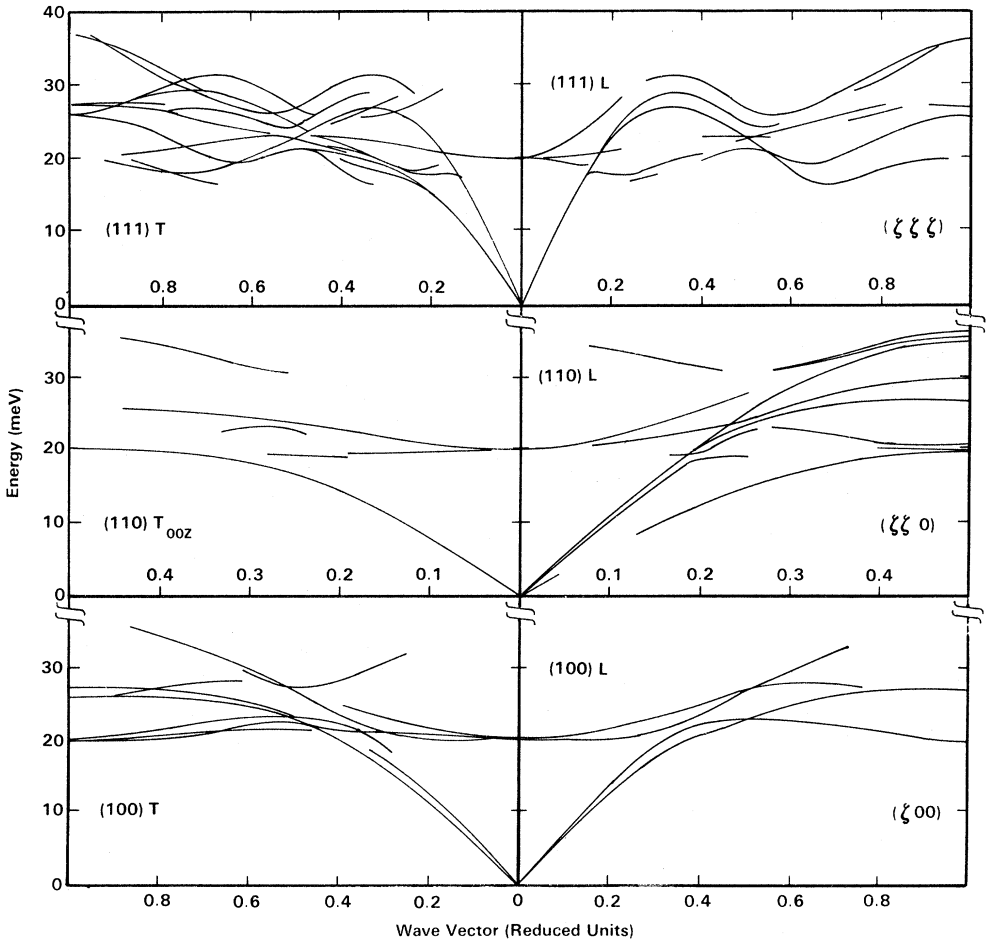

FIG. 1. Calculated phonon branches of β-phase NbD shown in the Brillouin zone of the bcc lattice of Nb.

(III) Since the symmetry of the orthorhombic structure of β-phase NbD is lower than the symmetry of the cubic host metal, some phonon branches which were degenerate in the cubic system are now split. This is true, in particular, for β-phase $NbD_{0.75}$, where defects in the D sublattice further reduce the symmetry. For some branches, this splitting of the acoustic branches can be observed in Fig. 1. At small wave vectors, the splitting is too small to be resolvable by inelastic neutron spectroscopy, and in an experiment will be observed as a broadening of the neutron groups.

(IV) From the large number of phonon branches showing up in some directions of Fig. 1, only the modes with the largest structure factors will be easily measurable. The other branches may only be observed as a high, structured background, or as shoulders and asymmetries in the shape of the measured neutron groups. The structure factors of some peaks are sensitive to the set of force constants used, especially near the zone boundaries. In the present calculation, the (110)L branch at the zone boundary proved to be most sensitive. From Fig. 1, a total of eight branches with energies between 20 and 35 meV can be seen at that point.

(V) Similar calculations have been performed for β-phase NbH by changing the hydrogen isotope mass (from 2 to 1 in amu) and the scattering length (from 6.7 to −3.7 in fm). The feature of the flat phonon branches at 20 meV has shown to be independent of the hydrogen isotope.

(VI) The large phonon structure factors for the branches at 20 meV are almost entirely due to the vibrations of the D atoms. This can be shown by setting the D scattering length to zero, in which case the calculated intensity of these modes drops at least one order of magnitude. Careful investigation of the eigenvectors revealed that the amplitude of the D motion for these flat modes was in general 1.5–2 times larger than for other

modes near the same energy. However, these amplitudes are still a factor of 2 to 3 smaller than the amplitudes of the D atoms for the high-frequency optic-mode excitations. This observation suggests a "resonant" enhancement of the D vibrations for particular modes in the acoustic frequency regime.

(VII) In a recent experiment on $NbH_{0.05}$, Lottner *et al.*[8] observed a broad inelastic peak at about 16 meV in the disordered α phase. Calculating the local vibrational spectrum for a single H defect using the Green's-function technique, the authors attributed this peak to a resonantlike H motion for a particular phonon mode.

Since an enhanced hydrogen amplitude causes an inelastic peak in the limit of low concentrations ($NbH_{0.05}$) as well as at high concentrations with long-range order of the D ($NbD_{0.75}$, $NbD_{1.0}$), it is probable that the peaks at about 19 meV observed by Shapiro *et al.*[2] in the α' phase can also be attributed to the same mechanism and/or to short-range order. In particular, it should be emphasized that there is no phase boundary between the α phase and the α' phase at high temperatures and that in disordered α'-phase $NbD_{0.85}$ only a fraction of all tetrahedral sites are occupied. The broadening of the peaks in the α' phase may be due to the increased disorder in this phase.

CONCLUSION

A simple lattice-dynamical model for β-phase NbD has been proposed, the main feature of which is to include the orthorhombic structure of the β phase and the multidomain nature of the crystals. This model suggests an explanation of the "flat phonon branches" at about 20 meV recently found experimentally as arising from large amplitudes of hydrogen or deuterium motion for particular modes in the β-phase structure. A similar explanation is suggested for the analogous α'-phase results.

In addition, the results presented here point up some difficulties inherent in the interpretation of a "dispersion relation" measured in a highly defected, multidomain sample. It appears that measurements on a single domain, nearly stoichiometric β-phase sample will be required in order to obtain unambiguous information about the lattice dynamics of this phase.

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[1]For a review, see T. Springer, *Investigation of Vibrations in Metal Hydrides by Neutron Spectroscopy in Hydrogen in Metals* I, Topics in Applied Physics, Vol. 28 (Springer, Berlin, 1978).

[2]S. M. Shapiro, Y. Noda, T. O. Brun, J. Miller, H. Birnbaum, and T. Kajitani, Phys. Rev. Lett. 41, 1051 (1978).

[3]S. M. Shapiro, D. Richter, Y. Noda, and H. Birnbaum, unpublished.

[4]Peaks observed at 10 meV in Ref. 2 have been shown to arise from higher-order scattering; S. M. Shapiro, D. Richter, Y. Noda, and H. Birnbaum, private communication.

[5]J. M. Rowe, N. Vagelatos, J. J. Rush, and H. E. Flotow, Phys. Rev. B 12, 2959 (1975).

[6]N. Stump, A. Magerl, G. Alefeld, and E. Schedler, J. Phys. F 7, L1 (1977).

[7]V. Lottner, A. Kollmar, T. Springer, W. Kress, H. Bilz, and W. D. Teuchert, in *Lattice Dynamics*, edited by M. Balkanski (Flammarion, Paris, 1978).

[8]V. Lottner, H. R. Schober, and W. J. Fitzgerald, Phys. Rev. Lett. 42, 1162 (1979).

[9]A. Rahman, K. Sköld, C. Pelizzari, S. K. Sinha, and H. E. Flotow, Phys. Rev. B 14, 3630 (1976).

[10]C. J. Glinka, J. M. Rowe, J. J. Rush, A. Rahman, S. K. Sinha, and H. E. Flotow, Phys. Rev. B 17, 488 (1978).

[11]V. A. Somenkov, A. V. Gurskaya, M. G. Zemlyanov, M. E. Kost, N. A. Chernoplekov, and A. A. Chertkov, Fiz. Tverd. Tela 10, 1355 (1968) [Sov. Phys.-Solid State 10, 1076 (1968)].

[12]M. A. Pick and R. Bausch, J. Phys. F 6, 1751 (1976).

[13]M. Born and K. Huang *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954), p. 246.