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Hydrogen local modes and phonon dispersion in $LuD_{0.19}$ and Lu

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The phonon dispersion of both pure Lu and α-$LuD_{0.19}$ is determined along the symmetry directions Γ-A and Γ-K-M. The phonon energies are partly found to increase due to hydrogen absorption. At low temperatures no influence of deuterium ordering on the phonon frequencies can be detected. Furthermore, the hydrogen local-mode properties are investigated in α-$LuD_{0.19}$. In accordance with recent results on α-$YH(D)_{0.18}$, the potential at the hydrogen site is found to be very anisotropic.

I. INTRODUCTION

In several hcp rare-earth metals like Sc, Y, Ho, Er, Tm, and Lu, hydrogen forms a solid solution phase (α phase) which is stable down to temperatures near 0 K.[1] The precipitation of the cubic dihydride phase occurs only at higher hydrogen concentrations, e.g., at 20 at. % in the case of lutetium. Within the solid solution phase the hydrogen atoms randomly occupy the tetrahedral interstitial sites.[2] The first indication for a structural change occurring in the α phase was a resistivity anomaly at lower temperatures found ten years ago,[3] characteristic features of which were recently elucidated in a diffuse neutron scattering experiment on $LuD_{0.19}$.[4] This earlier experiment revealed a chainlike structure consisting of pairs of deuterium atoms located on second neighbor sites along the hexagonal axis. A recent measurement of specific heat also showed an anomaly in the temperature range of deuterium ordering[5] and it was suggested that the phonon dispersion might stiffen due to the pair formation.

In the present work we investigate Lu and α-$LuD_{0.19}$ by inelastic neutron scattering. Thereby we want to explore to what extent the metal bonding is modified by hydrogen absorption. Since the phonon dispersion relations in pure Lu were unknown so far, our results also imply novel information about this element. The measurements on $LuD_{0.19}$ were carried out above and below the deuterium ordering temperature to examine the influence of the ordering process on the stiffness of the lattice. Motivated by recent observations of the hydrogen local mode in $YH(D)_{0.18}$, which revealed a surprising anisotropy of the potential at the tetrahedral interstice,[6] a special effort was devoted to the vibrational properties of the hydrogen atoms.

II. EXPERIMENTAL

The measurements were done on a conventional triple axis spectrometer (2 T) located at the thermal source of the Orphée reactor in Saclay. Cu(111) and pyrolytic graphite PG(002) were used as monochromator and as analyzer, respectively. Collimations for the phonon measurements were 50, 30, 49 and 49 min starting with the in-pile collimator. The hydrogen vibrations were investigated with a horizontally focusing monochromator and analyzer. The sample was a single crystal of Lu (purity 99.99%). After the phonon measurements in pure Lu the crystal was loaded with 19 at. % deuterium at 500 °C. The initial mosaic width was 30 min which increased somewhat upon hydrogen loading. The dispersion relations were determined in Lu and $LuD_{0.19}$ at room temperature. In $LuD_{0.19}$ also measurements as a function of temperature were performed.

III. PHONON DISPERSION

Phonon dispersion relations of Lu and $LuD_{0.19}$ are shown in Fig. 1. On the whole the dispersion curves of Lu resemble those of other rare-earth metals like Tb (Ref. 7) and Ho.[8,9] The phonon frequencies are about the same as in Ho, however, clearly higher than in Tb. For the most part hydrogen absorption induces a further increase of phonon energies. Especially the transverse acoustic branch along the hexagonal direction Γ-A-Γ and the longitudinal optic branch along Γ-K-M show a hardening of about 5–10 % in the entire Brillouin zone. This general frequency increase after hydrogen loading is at variance with the lattice softening expected if the effect of hydrogen on the metal lattice is described purely as a lattice expansion. The mode hardening observed indicates a change of interatomic interaction due to changes of the electronic structure with hydrogen loading.

There are several other metal-hydrogen systems where the changes of the phonon dispersion relations due to dissolved hydrogen have been investigated so far (for a review see, e.g., Ref. 10). In the bcc transition metals Nb, Ta, and V, hydrogen loading generally leads to a hardening of the lattice whereas in the fcc metal Pd a frequency decrease has been observed. Phenomenologically, therefore, $LuD_{0.19}$ might to some extent be related to the transition metal hydrides. However, in view of the different crystal structures involved and taking into account the stability of the disordered solution phase even at low temperatures, lutetium (and also yttrium) hydrides should be treated as a separate case. A comparison with CeD_{2+x} is even less straightforward since for low x this system is essentially an ordered phase (cerium dihydride) and an increase in x leads gradually to a loss of its metallic character.

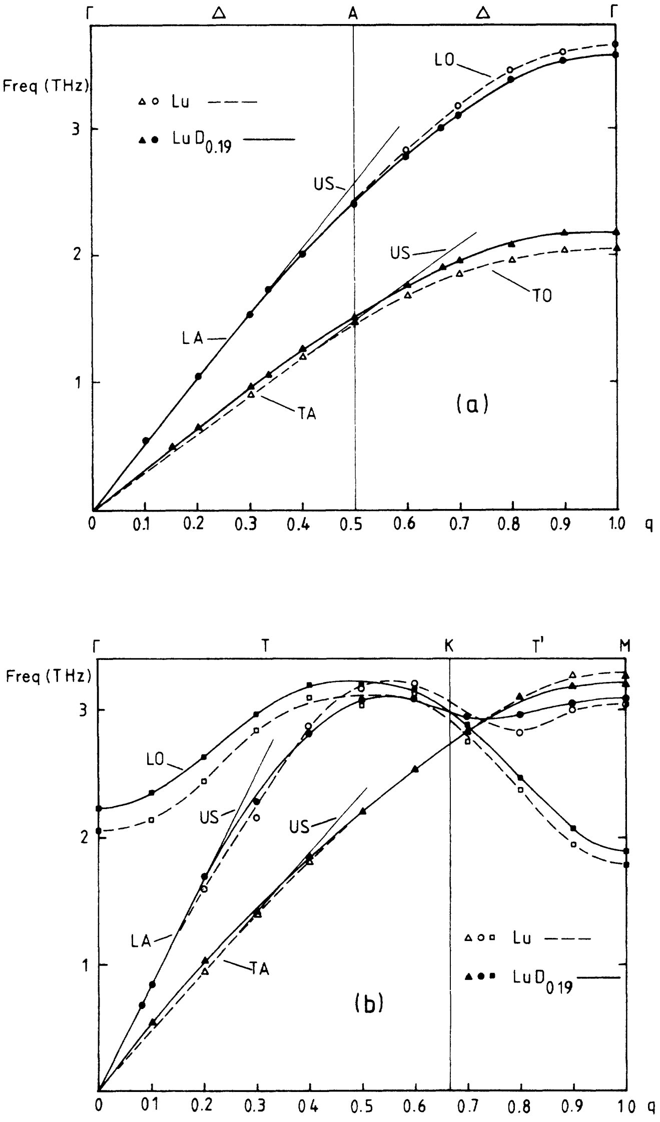

FIG. 1. Phonon dispersion curves for Lu and $LuD_{0.19}$. US denotes ultrasonic measurements in pure Lu. Lines are drawn to guide the eye. (a) Γ-*A*-Γ direction. (b) Γ-*K*-*M* direction.

The temperature dependence of phonon frequencies along Γ-*A*-Γ was investigated in $LuD_{0.19}$ between 300 and 120 K. The lower temperature is well below the range where hydrogen ordering occurs,[4] yet only small frequency changes were observed. The results were evaluated in terms of mode Grüneisen parameters

$$\gamma(q,j) = -\frac{\dfrac{\Delta\omega}{\omega}}{\dfrac{\Delta V}{V}}$$

and plotted in Fig. 2 (q is the reduced wave vector and j the branch index). The value for $\Delta V/V$ is 0.005. It should be noted, however, that the volume change is brought about primarily by a decrease of the lattice parameter along the hexagonal axis. The lattice parameter in the basal plane varies comparatively little within the temperature range investigated. Frequency changes determined for selected phonons along Γ-*K*-*M* yield qualitatively similar results. The hardening of a few percent at low temperature may well be explained by the normal behavior of an anharmonic solid as expressed by the Grüneisen relation. As a consequence, this frequency increase cannot explain the unusual temperature dependence of the specific heat reported in Ref. 5.

IV. DEUTERIUM LOCAL MODES

A search for the local mode energy was undertaken by constant Q scans from 30 to 110 meV at several positions in reciprocal space, but most extensively at Q=(0,0,6.9) on the hexagonal axis and at (4.2,0,0) in the basal plane.

The results obtained at 120 and 300 K are shown in Fig. 3. Similar to recent results[6] on $YD_{0.18}$ the present investigation on $LuD_{0.19}$ reveals strongly anisotropic vibrational characteristics of the hydrogen atom: for Q parallel to the hexagonal axis a much lower local mode

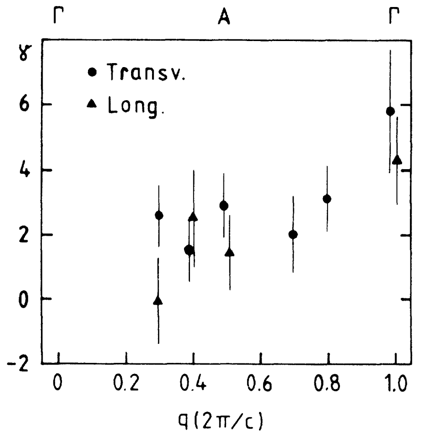

FIG. 2. Thermal mode Grüneisen parameters determined from phonon frequency shifts between room temperature and 120 K along Γ-*A*-Γ.

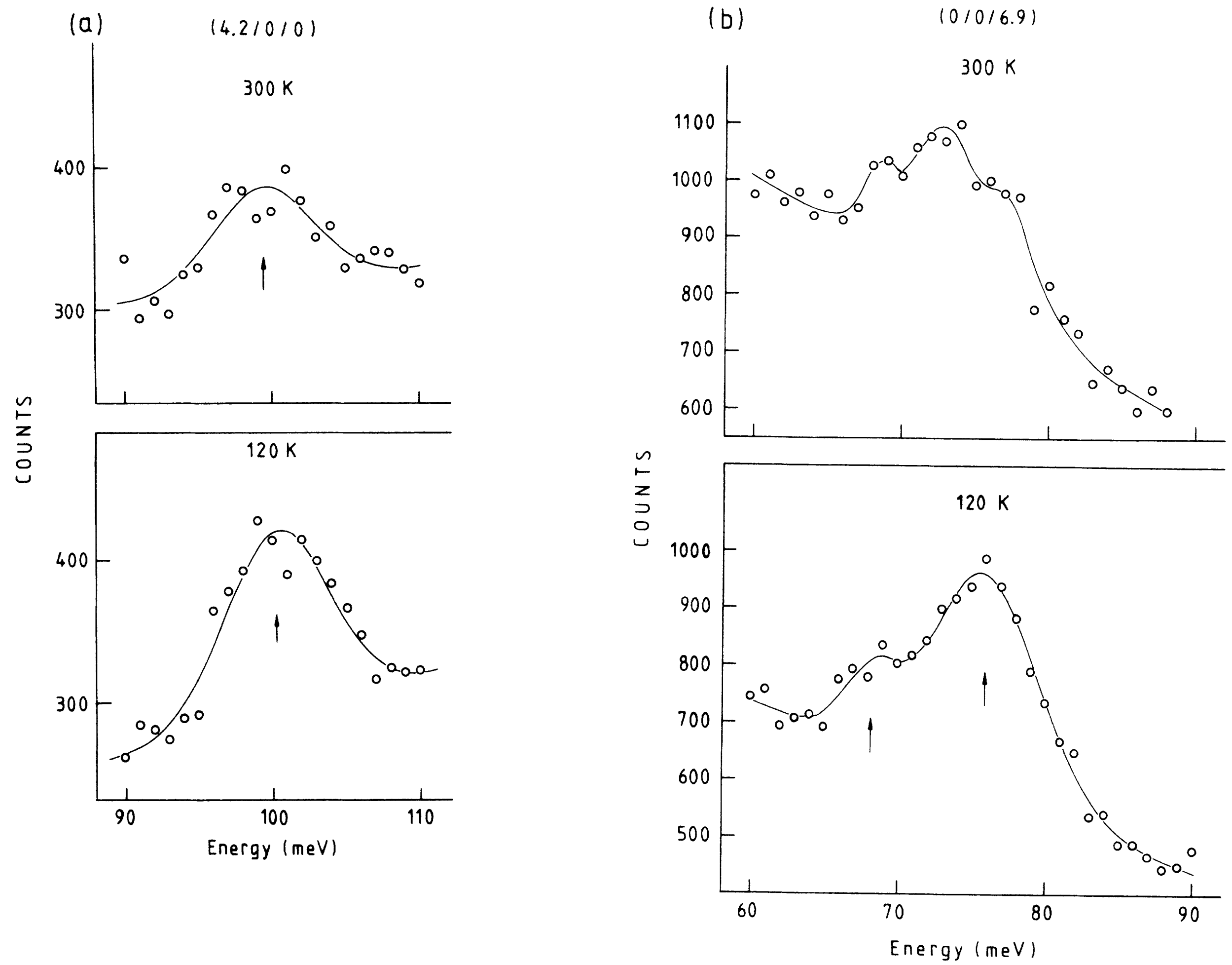

FIG. 3. Deuterium local modes at room temperature and at 120 K. The lines result from Gaussian fits. The maxima are indicated by arrows. (a) In the basal plane the data can be well described by one single vibrational frequency which is 99.5 meV at room temperature and 100.3 meV at 120 K. (b) Along the hexagonal axis the peak shape is split at 120 K, at room temperature the data suggest three different energy levels. Their exact positions, however, are somewhat arbitrary since a fit using three Gaussians is no more unique.

frequency is observed than for Q perpendicular to it. The anisotropy in $LuD_{0.19}$ exhibiting a frequency ratio near 1.4 between the hexagonal direction and the basal plane is even stronger than in $YD_{0.18}$. In order to investigate whether the different mode frequencies are due to a strong dispersion of the hydrogen vibration a further measurement was carried out at $Q=(0,0,6.0)$, however, the observed frequency was the same as that found at $Q=(0,0,6.9)$. Moreover, energy scans at $Q=(3,0,3)$, which lies between $Q=(0,0,6.0)$ and $Q=(4.2,0,0)$, gave two distinct peaks at the positions found previously for $Q=(0,0,6.9)$ and $(4.2,0,0)$.

An energy difference of comparable size between two vibrational modes is long known to occur for hydrogen atoms on tetrahedral interstices in the bcc transition metals Ta, Nb, and V. In these metals, however, the lattice points surrounding the interstice are considerably shifted relative to their positions in a regular tetrahedron and the "tetrahedral" sites in fact exhibit tetragonal symmetry. A relatively simple calculation based on central harmonic forces between first and second neighbors[11] immediately yields two energy levels differing by a factor of $\sqrt{2}$, in reasonable agreement with experiments.

In hexagonal lattices the metal atoms surrounding a hydrogen atom form perfect tetrahedra if the c/a ratio equals its ideal value $\sqrt{8/3}=1.633$. Deviations from this ratio reduce the symmetry of the tetrahedral interstitial sites and consequently remove the degeneracy of the hydrogen vibrational modes. In the case of pure lutetium c/a is about 1.585. It increases continuously upon loading with deuterium reaching values slightly above 1.59 for $LuD_{0.19}$. Hence, the resulting anisotropy is small and in the above approximation will give only a frequency splitting of a few percent for vibrations parallel and perpendicular to the hexagonal plane, respectively. On the other hand, the large difference between the two energy levels observed in $LuD_{0.19}$ clearly indicates a strongly anisotropic local-mode potential which is apparently much softer in the hexagonal direction than perpendicular to it. The soft potential along the c direction may be related to the fact that the distance to the next-neighbor tetrahedral site along this direction is only $\frac{1}{4}c$ without a metal atom in between. This geometrical arrangement suggests a low energy barrier between the two sites resulting in a softer vibration.

Similarly to the previous observation in $YD_{0.18}$ (Ref. 6) the intensity distribution observed at 120 K exhibits a split structure for **Q** parallel to the hexagonal axis. At room temperature the peak measured along the hexagonal direction may be composed of three energy levels. The third energy level appears between the split peak positions which decrease in intensity and become shoulders on either side of the intensity distribution. In agreement with Ref. 6 these findings can be interpreted in the following way. At very high temperatures the interaction between different hydrogen atoms is negligible and only one single mode frequency is present parallel to the c axis. At low temperatures the hydrogen atoms form pairs on next-nearest-neighbor positions along the c axis.[4] This arrangement gives rise to two different vibrational modes whose energies lie slightly below and above the frequency of an isolated hydrogen atom, respectively. Figure 3(b) shows the resulting split peaks at 120 K. At intermediate temperatures part of the hydrogen atoms no longer form pairs, thus leading to the appearance of the central frequency in Fig. 3(a) corresponding to the vibrations of isolated hydrogen atoms. In $LuD_{0.19}$, however, the three level structure is still present at 300 K, where in $YD_{0.18}$ one single peak is observed. From that we conclude that an appreciable amount of deuterium remains ordered in $LuD_{0.19}$ even at room temperature, thus implying a higher binding energy of the pairs.

V. SUMMARY

We have investigated vibrational properties of Lu and α-$LuD_{0.19}$ by inelastic neutron scattering. The main results are the following. In Lu metal the phonon dispersion is similar to that of other rare-earth metals like Tb and Ho. Hydrogen absorption induces a hardening of a few percent for part of the phonon branches but hydrogen ordering at low temperatures does not lead to an anomalous stiffening of the dispersion relation. Finally, in α-$LuD_{0.19}$ strongly anisotropic hydrogen local modes are observed exhibiting characteristics rather similar to those recently found in $YD_{0.18}$.

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