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Hydrogen vibration and phonon dispersion in α-ScD$_x$ systems

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The phonon dispersion relations in ScD$_x$ were determined by inelastic neutron scattering for $x = 0.19$ and $x = 0.33$. Predominantly, an increase of the acoustic-phonon frequencies is observed after hydrogen absorption. The hardening is most pronounced for the transverse-acoustic TA(002) phonon branch which in addition shows a shallow dip near $q = \frac{2}{3}$ especially at higher hydrogen concentration. An investigation of the deuterium local mode showed a strong vibrational anisotropy similar to recent results in YD$_{0.19}$ and LuD$_{0.19}$. However, in contrast to YD$_{0.19}$ and Lu$_{0.19}$ no peak splitting was observed for the deuterium local mode polarized in the hexagonal direction especially at low temperatures where the formation of D pairs is fully developed. This indicates that a direct D-D interaction is not essential for the pair formation.

I. INTRODUCTION

Some rare-earth elements such as Er, Ho, Sc, Y, and Lu form with hydrogen a solid-solution phase up to rather high hydrogen concentration which is stable down to temperatures near 0 K.[1] A resistivity anomaly found ten years ago was the only indication for some structural change occurring within the solid-solution phase.[2] Recently, a neutron scattering investigation revealed in LuD$_{0.19}$ a chainlike ordering of hydrogen pairs along the hexagonal c direction.[3] Within a pair the hydrogen atoms are located along c on second-neighbor tetrahedral interstitial sites. This chain formation was corroborated in a more extensive investigation in two scattering planes in LuD$_x$ (Ref. 4) and was further found in the α-ScD$_x$ system.[5] A similar linear hydrogen ordering tendency was also reported for YD$_x$.[6]

The chainlike hydrogen ordering in both LuD$_x$ and ScD$_x$ systems could be explained in terms of a lowering of coherency stresses within the hexagonal matrix.[4,5] If hydrogen pairs are described as elastic dipoles the linear structure appears as a favorable arrangement within the hexagonal matrix having cylindrical elastic symmetry.

Whereas, the long-range morphology of the chain formation can be explained by elastic interactions, the individual pair formation within a chain is still an open question. It may be either of electronic origin or due to an elastic attraction. An investigation of vibrational properties of the deuterium local mode, first in YD$_{0.19}$ (Ref. 7) and then in LuD$_{0.19}$ (Ref. 8) revealed an astonishingly strong anisotropic potential at the tetrahedral site: The frequency of the vibration along the c direction is by a factor of about $\sqrt{2}$ lower than in the basal plane. Furthermore, the hydrogen local mode along the c direction showed a peak splitting at low temperatures, indicating the presence of a direct D-D interaction in the paired state. As the two D atoms forming a pair are separated by a metal atom, the D-D interaction has to be mediated by the conduction electrons which favor an electronic effect as driving mechanism for the pair formation. In the present paper we describe a neutron scattering investigation of the vibrational properties of the ScD$_x$ system. As in ScD$_x$ the solid-solution hydrogen phase exists over a wide concentration range ($x \sim 0.35$),[9] the influence of hydrogen on the lattice dynamics could be investigated at different concentrations within a single-phase region. In the first part of the paper we present measurements of the acoustic phonon dispersion in ScD$_x$. Thereafter we describe the deuterium local mode properties in ScD$_x$ and discuss the differences to previous results for YD$_x$ and LuD$_x$.

II. EXPERIMENT

The measurements were done on the triple-axis spectrometer ($2T$) located at the thermal source of the Orphée reactor in Saclay. Cu(111) and pyrolytic graphite PG(002) were used as monochromator and analyzer. The collimations starting with in-pile were 50, 30, 49, and 49 min. The measurements of the local mode were done with a horizontally focusing monochromator and analyzer. Two crystals of Sc (purity 99.99%) were loaded at 500 °C with 19 at. % and 33 at. % deuterium, respectively. The mosaicity of the loaded crystals was about 60

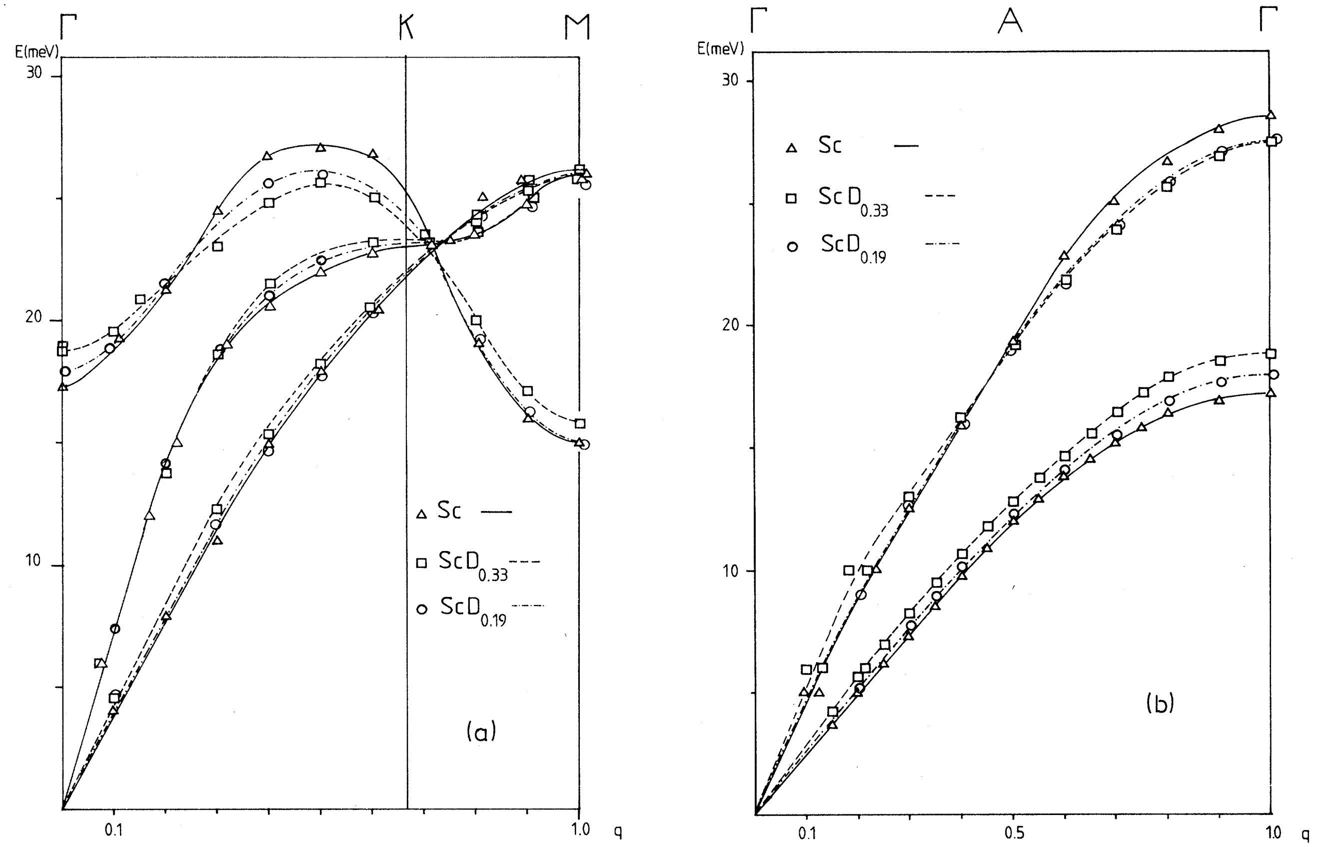

FIG. 1. (a) Phonon dispersion relations at room temperature in the Γ-*K*-*M* direction: solid line (△) pure Sc, dashed line (□) $ScD_{0.33}$, and dashed-dotted line (○) $ScD_{0.19}$. The lines are guides to the eye. (b) Phonon dispersion relations at room temperature in the Γ-*A*-Γ direction. The symbols are the same as in (a).

min. Measurements were done from room temperature down to 10 K.

III. ACOUSTIC PHONONS IN ScD_x

The phonon dispersion relations of Sc, $ScD_{0.19}$, and $ScD_{0.33}$ were determined at room temperature in two symmetry directions, i.e., in the hexagonal Γ-*A*-Γ direction and in the basal plane Γ-*K*-*M*. The results are shown in Fig. 1. The dispersion curves for pure Sc determined in this experiment are in good agreement with results from Ref. 10.

Figure 1 shows that hydrogen loading even with rather high concentrations of $x=0.33$ induces only small changes in the phonon branches. Predominantly, a tendency towards a frequency hardening is observed especially for long-wavelength phonons. The strongest changes are seen in the transverse-acoustic branch in the hexagonal direction TA (002) where a frequency hardening of about 10% is observed for $x=0.33$. Moreover, a softening of longitudinal phonons near the *K* point and in the Γ-*A*-Γ direction near the Brillouin-zone boundary can also be noticed. Considering generally the hydrogen influence on the phonon dispersion the present results on ScD_x are qualitatively similar to that recently described for LuD_x.

During the course of this investigation we became aware that the hydrogen-induced frequency increase of the TA [002] acoustic-phonon branch was not uniform over the whole Brillouin zone. Therefore we investigated this branch in more detail. Figure 2 shows that the relative frequency increase upon hydrogen loading has a minimum near the reduced q value of $\frac{2}{3}$ for $x=0.19$ and

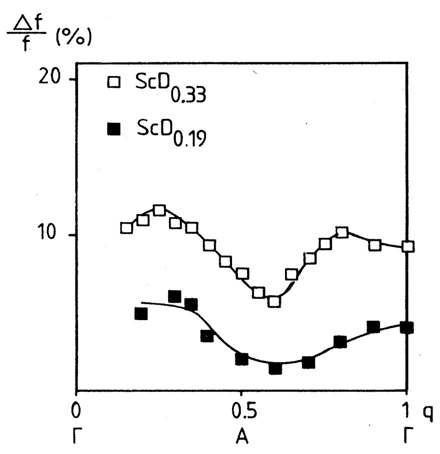

FIG. 2. Relative phonon frequency change at room temperature upon hydrogen loading for the transverse-acoustic phonon branch TA(002) in the hexagonal Γ-*A*-Γ direction. □, $ScD_{0.33}$ and ■, $ScD_{0.19}$.

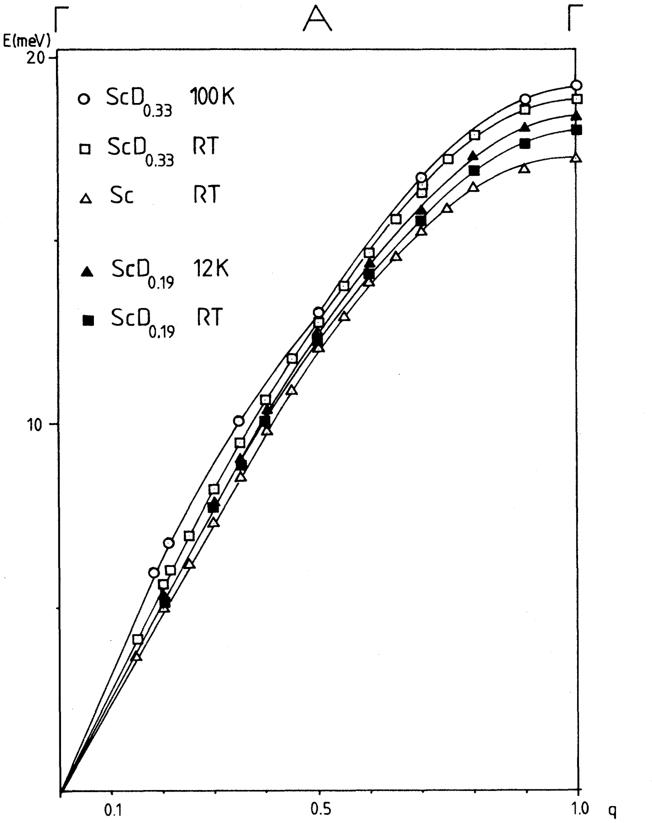

FIG. 3. The transverse-acoustic TA(002) branch for Sc, $ScD_{0.19}$, and $ScD_{0.33}$ at different temperatures. ○, $ScD_{0.33}$ at 100 K; □, $ScD_{0.33}$ at room temperature; △, Sc at room temperature; ▲, $ScD_{0.19}$ at 12 K; ■, $ScD_{0.19}$ at room temperature.

$x = 0.33$ and that the minimum is more pronounced for the higher concentration.

At low temperature generally a frequency increase by a few percent compared to room temperature occurs which is quite normal for an anharmonic solid. Figure 3 shows the TA (002) branch in more detail. The general frequency hardening with hydrogen loading is clearly observed but the dip in the relative frequency increase (of a few percent) shown in Fig. 2 is not seen in this scale. Only the phonon branch for the $ScD_{0.33}$ system at 100 K may reflect in Fig. 3 the presence of a dip near $q \sim \frac{2}{3}$. The dip therefore seems to be more pronounced at low temperatures in $ScD_{0.33}$. It should be noticed that the results of Fig. 2 do not correspond to a phonon softening, of course, but mean a dip in the frequency increase induced upon hydrogen loading.

IV. DEUTERIUM LOCAL MODE

In search for the local mode frequency constant Q scans were done at the reciprocal lattice positions $Q = (0.0,6)$ in the hexagonal direction and at $Q = (4.2,0,0)$ in the basal plane. Figure 4 shows the results for the two deuterium concentrations. A strong anisotropy of the local mode frequencies is found. The vibration in the hexagonal direction is much softer than in the basal plane with a frequency ratio of about $\sqrt{2}$. This result is similar to what has been found in YD_{19} and LuD_{19} (Refs. 7 and 8) but the vibration frequencies are by a few percent higher (5%).

In both $ScD_{0.19}$ and $ScD_{0.33}$ the local modes were also investigated at low temperatures where the hydrogen ordering and consequently the pairing is fully developed. The results are also shown in Fig. 4. No peak splitting was found for both concentrations. Moreover, Figs. 4(a) and 4(b) show that the hydrogen vibration frequency shifts slightly towards higher energies with increasing D concentration.

The energy resolution of the spectrometer was measured and the results are plotted as horizontal bars in Fig. 4. For comparison the previous data for $LuD_{0.19}$ are also shown [Fig. 4(d)]. It appears that the measured width of the local mode polarized in the hexagonal direction is by about 30–40 % broader than the resolution. Considering that the measured width is a convolution product with the resolution an intrinsic linewidth of the local mode of about 5 meV is obtained. The same resolution bar plotted in the results for $LuD_{0.19}$ shows that a single component of the split energy levels is also broader than the resolution by approximately the same amount as found in ScD_x. Therefore, a similar intrinsic width of the individual energy component is found in both systems. A comparison of LuD_x and ScD_x therefore seems to indicate that the second level is indeed absent in ScD_x. It follows that a direct D-D interaction is much smaller or absent in the ScD_x system. In view of these peak characteristics, indicating a similar intrinsic linewidth for both systems an upper limit of about 2 meV for a possible underlying local mode splitting in ScD_x may be estimated.

V. DISCUSSION

The investigation of the deuterium local mode in the ScD_x system has revealed a similar anisotropy of the vibrational properties of the hydrogen atom as previously found in YD_x and LuD_x. The softer hydrogen vibration in the hexagonal c direction in the solid solution phase of all three metal-hydrogen systems is probably connected to the close vicinity of the adjacent tetrahedral interstice inducing a soft potential. On the other hand, the local mode frequencies in ScD_x are higher than in YD_x and LuD_x, respectively. This may be related to the smaller volume of the Sc unit cell producing a steeper potential at the tetrahedral site.

In view of the ordering phenomena in rare-earth hydrogen systems the most important result of the present investigation is the lack of evidence for a direct D-D interaction in the "paired" hydrogen state in ScD_x for both concentrations. This indicates that a direct D-D interaction is not a necessary condition for pair formation and therefore favors a pairing mechanism by elastic interaction.

The observed acoustic-phonon hardening is at variance with the frequency decrease expected if the hydrogen action on the metal lattice is taken purely as a lattice expansion. On the other hand, it is known that in rare-earth hydrogen systems the electron density of states at the Fermi level is decreased with hydrogen loading which finally induces a transition to a saltlike ionic compound

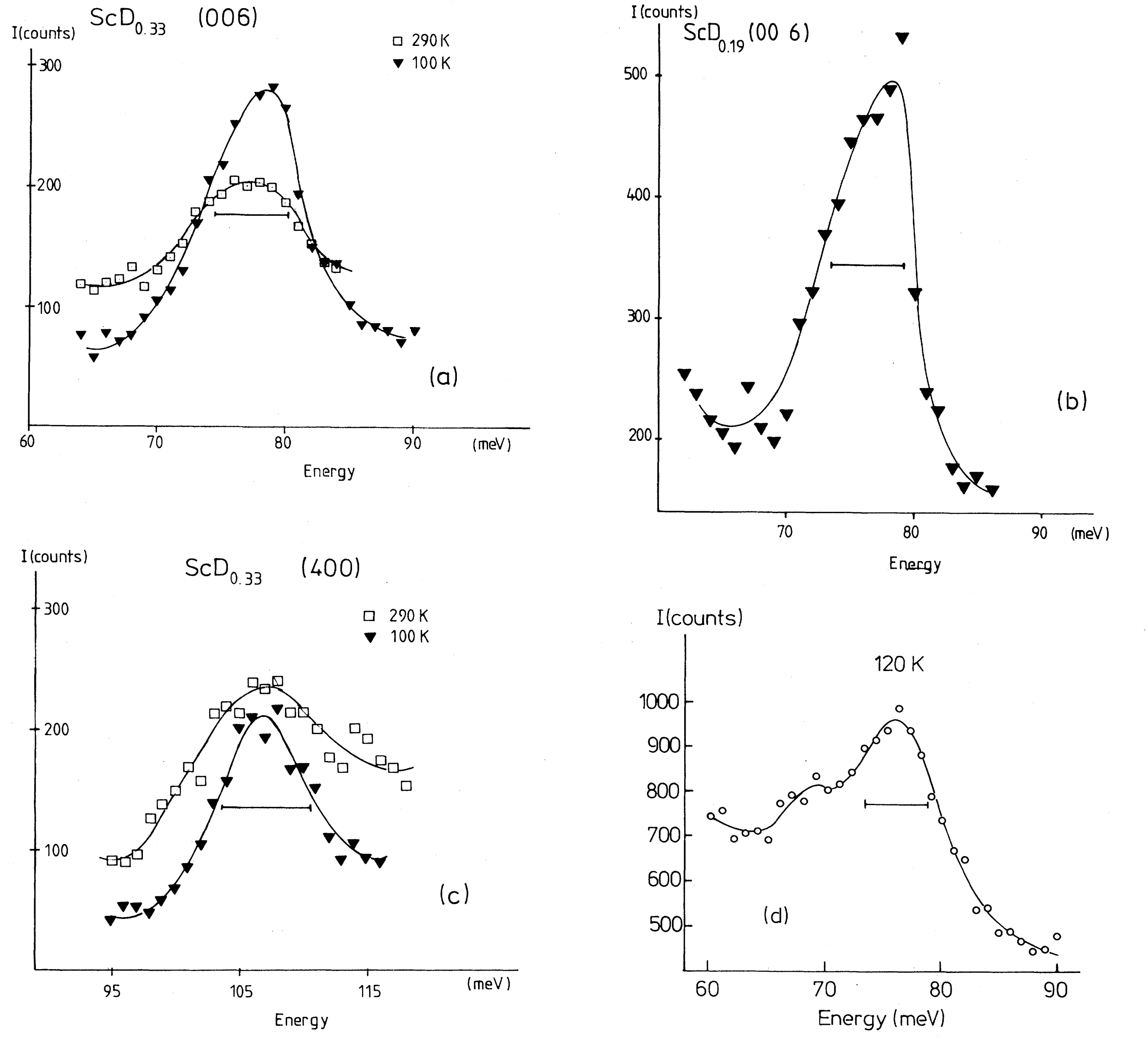

FIG. 4. (a) Hydrogen local mode as observed in the hexagonal Γ-*A*-Γ direction in $ScD_{0.33}$. □, 290 K; ▼ 100 K. (b) Hydrogen local mode as observed in the hexagonal Γ-*A*-Γ direction in $ScD_{0.19}$ at 100 K. (c) Hydrogen local mode as observed in the basal plane [(Γ-*K*-*M*) direction] in $ScD_{0.33}$. □, 290 K; ▼, 100 K. (d) For comparison, the split hydrogen local mode in the Γ-*A*-Γ direction in $LuD_{0.19}$ at 120 K (Ref. 8).

at high hydrogen concentrations ($x>2$).[11] The frequency hardening observed in ScD_x for the acoustic phonons and also for the D local mode may be connected with this decrease of the electron density resulting in a weaker shielding of the ionic potentials and consequently an increase of the atomic force constants. The hydrogen-induced softening of some longitudinal phonons near the *K* point and the Brillouin-zone boundary may reflect changes in atomic force constants of longer range.

Finally, the present investigation revealed a shallow dip in the transverse acoustic TA(002) phonon branch at about $q=\frac{2}{3}$. This dip can be already seen in $ScD_{0.19}$ but is more pronounced in $ScD_{0.33}$ where the system is close to the hexagonal cubic ($\alpha-\beta$) phase boundary. A similar dip, although less developed can be seen in $LuD_{0.19}$.[8] We do not know the origin of this hydrogen-induced phonon anomaly. But it is interesting to note that this dip occurs at a q value geometrically compatible with a transformation shear wave along the c direction leading to a change from the hexagonal *AB* to the fcc *ABC* stacking sequence. Generally phonon anomalies have been found as precursors of Martensitic phase transitions[12] and the observed dip in ScD_x may be a lattice dynamical precursor to the hcp-fcc phase transition occurring near

$x \sim 0.35$.

In summary, the hydrogen vibration in ScD_x shows a similar anisotropy as recently described for LuD_x and YD_x, but no split energy levels are observed even at low temperatures where hydrogen pairing is well developed. For the acoustic phonons hydrogen absorption predominantly induces a frequency increase similar to what was found in LuD_x.

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