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# Lattice vibrations and electronic transitions in the rare-earth metals: yttrium, gadolinium and lutetium

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## Abstract

Lattice vibrations in high-pressure phases of Y, Gd and Lu were studied by Raman spectroscopy. The observed phonon frequencies decrease towards the transitions to the dhcp and fcc phases. There is evidence that the entire structural sequence hcp  $\rightarrow$  Sm-type  $\rightarrow$  dhcp  $\rightarrow$  fcc under pressure for the individual regular rare-earth metals and along the lanthanide series at ambient pressure involve softening of certain acoustic and optical phonon modes and of the elastic shear modulus  $C_{44}$ . Comparison is made to transitions between close-packed lattices in other metals, and possible correlations to s–d electron transfer are discussed.

## 1. Introduction

The regular lanthanides (from La to Lu excluding Ce, Eu and Y6) exhibit a common initial structural sequence hcp  $\rightarrow$  Sm-type  $\rightarrow$  dhcp  $\rightarrow$  fcc  $\rightarrow$  distorted fcc, which is observed both with increasing pressure for the individual members and at ambient conditions along the lanthanide series with decreasing atomic number [1]. As shown by Duthie and Pettifor [2], this sequence is due to an increase in d-electron character of the conduction band, s  $\rightarrow$  d electron transfer, which occurs both under pressure and with decreasing atomic number at normal pressure.

Lattice vibrations contribute to many thermodynamic parameters, are related to elasticity, and play a crucial role in certain types of phase transitions. Therefore, knowledge of lattice dynamics is essential in understanding many properties of solids. The phonon frequencies are determined by the interatomic forces, which are controlled to a large extent by the electronic structure in metals. Since the similarities in the electronic structure of the regular lanthanides are responsible for their systematic structural behaviour [3], it is reasonable to expect common trends also in their lattice dynamical behaviour. This was indeed noticed in previous high-pressure studies of lattice vibrations in some lanthanides, which revealed a negative pressure

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shift of the transverse optic (TO)  $E_{2g}$  mode of the hcp phase as the transition to the Sm-type structure is approached [4]. Recently it has been recognized that this transition is also associated with a weakening of the elastic modulus  $C_{44}$  [5].

Theoretical lattice-dynamical investigations of the rare-earth metals at high pressure are not available at present, and there is also a lack of phonon data of the high-pressure phases—experimental phonon-dispersion curves of regular lanthanides at normal pressure are limited to Y, Lu, Ho, Tb in the hcp phase and fcc-La [6–11]—indicating that the present knowledge of the lattice-dynamical behaviour of the lanthanides is incomplete and far from being understood. The present paper approaches the lattice-dynamics of post-hcp close-packed phases of the regular lanthanides by high-pressure Raman spectroscopy of Gd and Lu as well as Y, the latter element being known to behave like a regular lanthanide in the considered pressure range [1, 3].

## 2. Experimental details

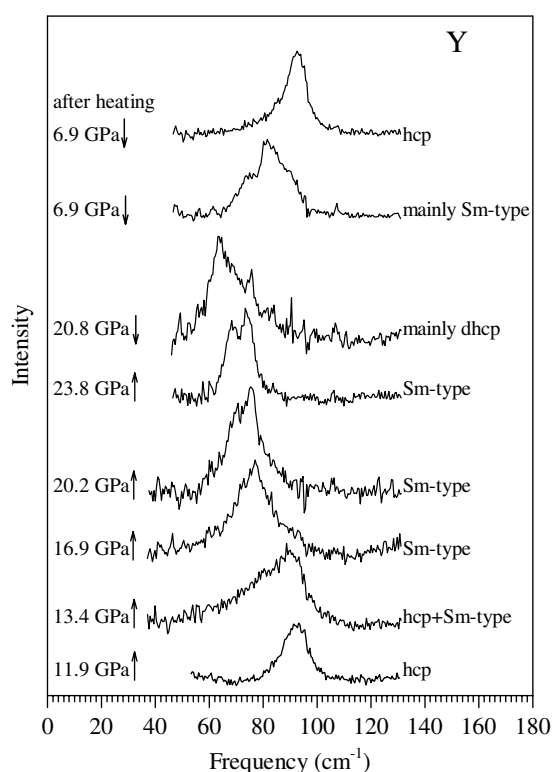
Raman studies were made on polycrystalline samples using a high-pressure diamond-anvil cell. The samples were provided by W B Holzapfel and detailed chemical analysis has been given in [12]. Raman spectra were excited with the 647 nm line of a  $Kr^+$  laser focused down to  $\approx 10 \mu\text{m}$ . The scattered light was analysed at an angle of  $135^\circ$  with respect to the incoming laser beam using a 0.6 m triple spectrograph and a liquid-nitrogen-cooled CCD multichannel detector. A 4:1 methanol:ethanol mixture was used as the pressure transmitting medium. The pressure was determined by the ruby fluorescence method [13].

## 3. Results

The hcp lattice with space group  $D_{6h}^4 (P6_3/mmc)$  has two atoms per unit cell that are located on sites of symmetry  $D_{3h}$ . From the six normal modes of zero wavevector the doubly degenerate  $E_{2g}$  is Raman active. The Sm-type lattice belongs to space group  $D_{3d}^5 (R\bar{3}m)$  and has 3 atoms per unit cell, one of which is located on a site of symmetry  $D_{3d}$  and the remaining two atoms have site symmetry  $C_{3v}$ . There are nine normal modes of zero wavevector and the two Raman active modes,  $A_g$  and  $E_g$ , derive from the atoms on the  $C_{3v}$  site. The dhcp lattice, space group  $D_{6h}^4 (P6_3/mmc)$ , has four atoms per unit cell on sites of symmetry  $D_{3h}$  and one mode, the doubly degenerate  $E_{2g}$  mode, shows Raman activity.

### 3.1. Yttrium

At room temperature the phase transitions in the lanthanides occur very sluggishly, and they are associated with large hysteresis effects [12]. In x-ray diffraction studies of Y, the hcp  $\rightarrow$  Sm-type phase transition has been observed around 15 GPa, the transition to dhcp in the pressure range 28–34 GPa, and the distorted fcc lattice becomes stable above 45 GPa [14, 15]. In down-stroke runs the dhcp lattice could be retained down to approximately 10 GPa, where a transition directly from dhcp to hcp has been observed [16]. As can be noticed from the spectra in figure 1, in Raman spectroscopy the transition to the Sm-type structure is connected with the appearance of a new Raman band approximately  $8 \text{ cm}^{-1}$  below the  $E_{2g}$  mode of the hcp phase, which occurs around 14 GPa in Y in the present study. Above 20 GPa a doublet structure could be clearly resolved for this band, in agreement with the group theoretical prediction of two Raman active modes for the Sm-type structure. This doublet shifts to lower frequencies on pressure increase and has been observed up to 27.3 GPa. At the maximum pressure of 32.3 GPa a very weak single peak could be observed at  $60 \text{ cm}^{-1}$ , the pressure dependence of which, taken during pressure release, is different from that of the Sm-type phase modes. This

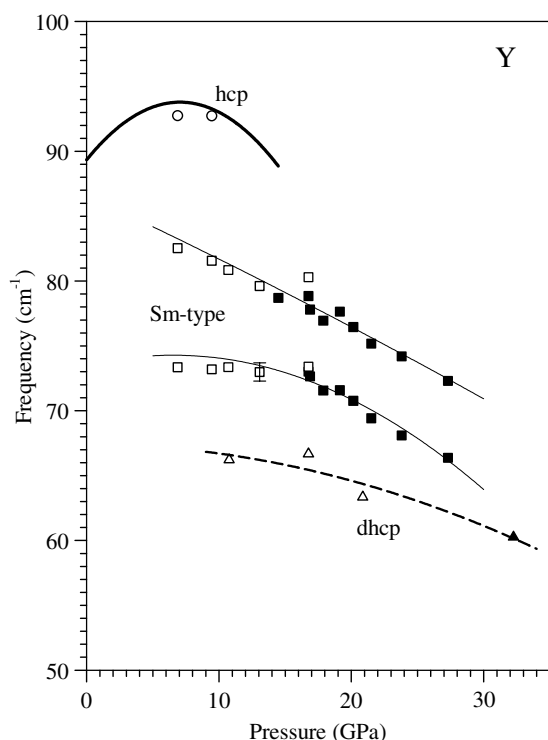


**Figure 1.** Raman spectra of various phases of Y. Upward arrows indicate pressure increase and downward arrows indicate pressure decrease. Note that the spectrum at 20.8 GPa was obtained by unloading from 32.3 GPa.

mode is therefore assigned to the dhcp phase. The dhcp phase was observed as the dominant phase down to 20 GPa, a phase mixture with increasing Sm-type content was observed on further pressure decrease, and at 4.8 GPa the back transition to hcp was nearly completed. The back transition to hcp could also be initiated at higher pressures, e.g. at 7 GPa, when the laser power was increased resulting in a higher sample temperature. The pressure dependence of the observed Raman modes is summarized in figure 2, which reveals that negative pressure shifts are observed for all Raman modes as the phase transitions are approached.

### 3.2. Gadolinium

High-pressure x-ray diffraction studies have shown that the Sm-type structure is difficult to obtain purely at room temperature in Gd [16]. Transitions from hcp or phase mixtures (hcp + Sm-type) with dominant hcp portions to dhcp have been observed in the pressure range 7–9 GPa [12, 15–19]. A similar behaviour is also observed in the Raman spectra of Gd, a typical set of which, obtained during loading, is shown in figure 3 (spectra (a)–(e)). Above 2 GPa the hcp mode becomes increasingly asymmetric on the low-frequency side, indicating the coexistence of a new phase. A further change in the spectral features occurs above 8 GPa, where the intensity of the hcp peak strongly decreases and the Raman spectrum contains one peak. This peak could be monitored on further pressure increase and also during unloading down to 2 GPa. Below 2 GPa the hcp peak reappeared (figure 3, spectrum (h)). Since dhcp is the stable phase of Gd above 10 GPa, this low-frequency peak must be assigned to the dhcp phase. However, not all of the spectral features with frequencies lower than that of the hcp peak, which were observed during pressure increase up to 7 GPa, can be attributed to the dhcp phase,



**Figure 2.** Pressure shift of Raman modes in various phases of Y. Thick solid curve: hcp [4]; thin solid curve: Sm-type; dashed curve: dhcp; solid symbols: loading; open symbols: unloading. The lines serve as guides for the eye.

since their frequencies are higher than those of the dhcp mode, and must therefore originate from the Sm-type phase. This is clearly demonstrated in figure 3 (spectra (f) and (g)), where a spectrum obtained during pressure release at 4.2 GPa (hcp + dhcp) is compared to a spectrum at 3.84 GPa, obtained on pressure increase and with the hcp peak subtracted. An increase of the portion of the Sm-type phase could be obtained when the temperature of the sample spot was raised by increasing the laser power. The Sm-type structure allows two Raman active modes, and from the studies of Y it is known that the Sm-type Raman modes have frequencies between those of the hcp and dhcp mode. For Gd the hcp and dhcp frequencies are closer together than in Y, which means that the two Sm-type modes are difficult to resolve. The low-frequency asymmetry, observed for the hcp-subtracted spectrum at 3.8 GPa in figure 3, indicates a doublet structure of the Sm-phase band. Since the transition to dhcp occurs at higher pressures, it is reasonable to assume that no dhcp admixtures are present, and this feature can be entirely attributed to the Sm-type phase. The frequencies of the second mode of the Sm-type structure and those of the dhcp mode are close together in Gd. In one run hcp portions could be observed up to 13.6 GPa, giving further evidence for the sluggishness of these phase transitions. The pressure shifts of the various modes are collected in figure 4, where one can notice that all modes shift to lower frequencies with increasing pressure.

### 3.3. Lutetium

For Lu, the transitions hcp  $\rightarrow$  Sm-type  $\rightarrow$  dhcp have been observed around 25 and 38 GPa, respectively, in room temperature x-ray diffraction studies during pressure increase [12, 15, 16]. In the present Raman study a new peak 9 cm<sup>-1</sup> below the hcp peak indicates the transition to Sm-type structure around 20 GPa (figure 5). This peak could be observed down to 5 GPa on pressure release, where the transition back to hcp occurs. Above 12 GPa this mode exhibits a slightly

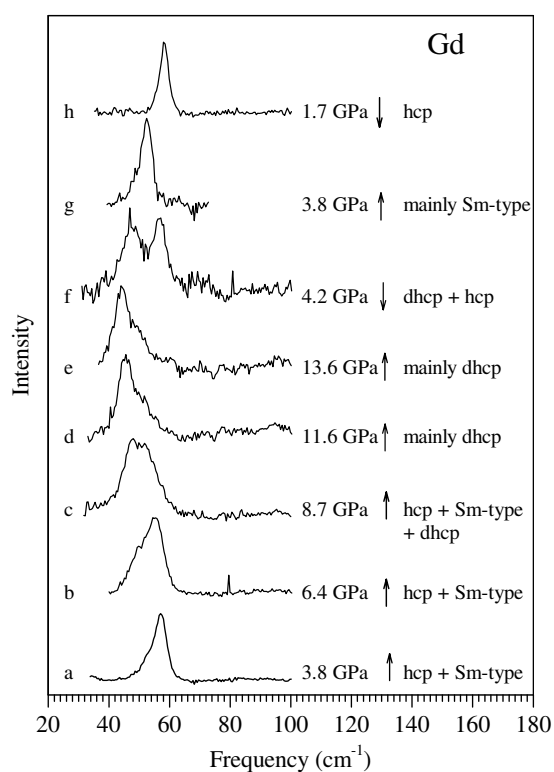
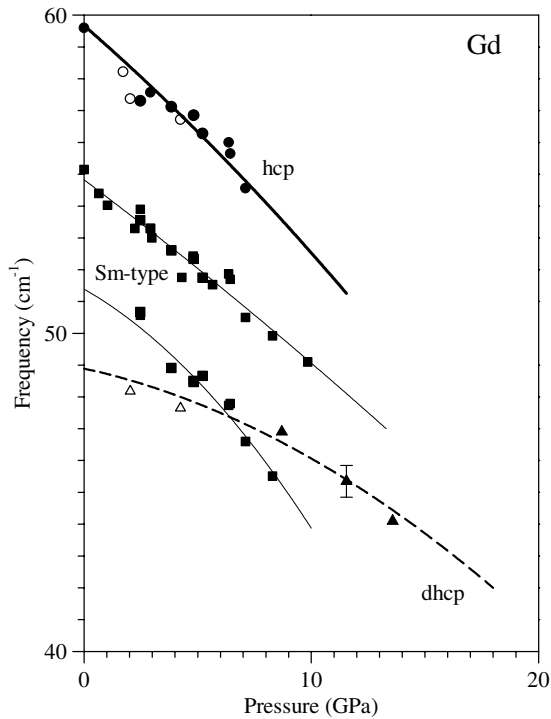


Figure 3. Raman spectra of various phases of Gd.

negative frequency shift with increasing pressure. A second mode with lower frequency, which shows nearly no frequency shift in the investigated pressure range (figure 6), has also been noticed.

#### 4. Discussion

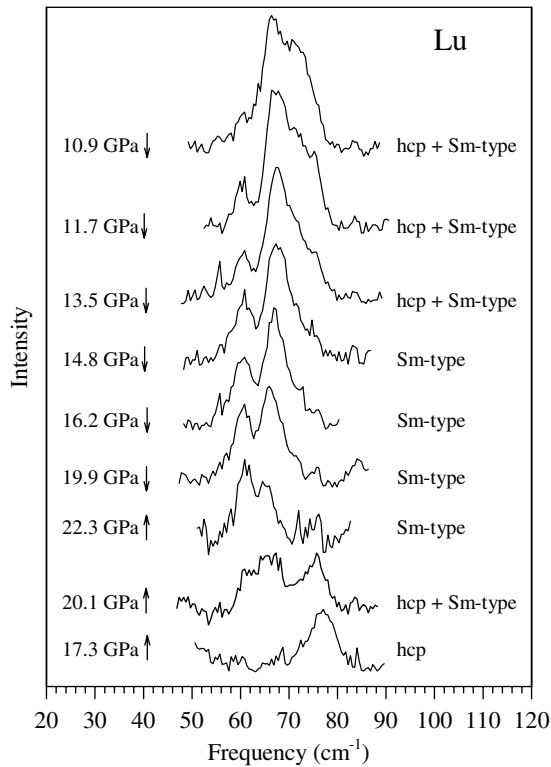
Comparison of the frequency shifts of the observed modes shows the same qualitative behaviour under pressure for all three rare-earth metals. Not only the hcp  $\rightarrow$  Sm-type transitions, but the whole sequence hcp  $\rightarrow$  Sm-type  $\rightarrow$  dhcp  $\rightarrow$  fcc involve a decrease of the observed mode frequencies. On constructing their generalized phase diagram for the regular lanthanides, Johansson and Rosengren [20] introduced the ratio of the Wigner–Seitz radius  $R_{WS}$  to the ionic radius  $R_I$  (Johansson–Rosengren parameter), which puts the results for the individual metals under pressure and along the lanthanide series at normal pressure on a common footing: the radius ratio decreases both under pressure and with decreasing atomic number along the series. They noticed that the regular structural transitions are well characterized by one critical value of this radius ratio for each transition. In figure 7 the mode frequencies for normal pressure, multiplied by the square root of the atomic masses to account for the effect of the different masses, are shown as a function of the radius ratio. In this representation the frequency shifts within the lanthanide series at ambient conditions show the same qualitative behaviour as for the individual members under pressure, i.e., mode softening also occurs along the lanthanide series.



**Figure 4.** Pressure shift of Raman modes in various phases of Gd. Thick solid curve: hcp [4]; thin solid curve: Sm-type; dashed curve: dhcp; solid symbols: loading; open symbols: unloading. The lines serve as guides for the eye.

For hexagonal crystals the frequency of the TO mode is directly proportional to the square root of the elastic shear modulus  $C_{44}$  [24, 25], which implies that these phase transitions are associated with a decrease of  $C_{44}$  [5]. A lowering of  $C_{44}$  can also be noticed for the regular lanthanides at ambient pressure along the structural sequence hcp  $\rightarrow$  Sm-type  $\rightarrow$  dhcp  $\rightarrow$  fcc, which is also shown in figure 7. The elastic constant  $C_{44}$  determines the dispersion of the transverse acoustic (TA) branch along certain directions in hexagonal crystals. A decrease of  $C_{44}$  is equivalent to a decrease of the slopes of these acoustic branches, i.e., acoustic phonons also exhibit a negative frequency shift in the lanthanides under compression. Evidence for such a behaviour has been provided previously by ultrasonic studies, in which softening of transverse and longitudinal acoustic phonons was observed in Pr and La in association with the dhcp  $\rightarrow$  fcc and fcc  $\rightarrow$  distorted fcc phase transitions and has been related to special aspects of the s-d transfer [30].

The low-pressure phases of the regular rare-earth metals in general are characterized by very low lattice Grüneisen parameters, which have been attributed to the electronic s-d transition softening [31]. The optical modes, investigated here, and the related acoustic branches with their low and negative mode Grüneisen parameters, contribute to these low lattice Grüneisen parameters and the unusually low mode Grüneisen parameters for Y and Lu with  $\gamma(E_{2g}) \approx 0.6-0.7$  at normal pressure far away from the phase transitions, as compared to normal values which range approximately from 1.3 to 2.3 [32, 33], would be in accord with softening arising from s-d electron transfer, which is under way already at ambient pressure in these metals. Therefore, it is tempting to relate the observed anomalies to the special electronic structure of the lanthanides and its changes under compression or along the lanthanide series at ambient conditions. In this context it is interesting to note that recent theoretical studies of Cs have suggested that the s-d transition leads to softening and dynamical instabilities

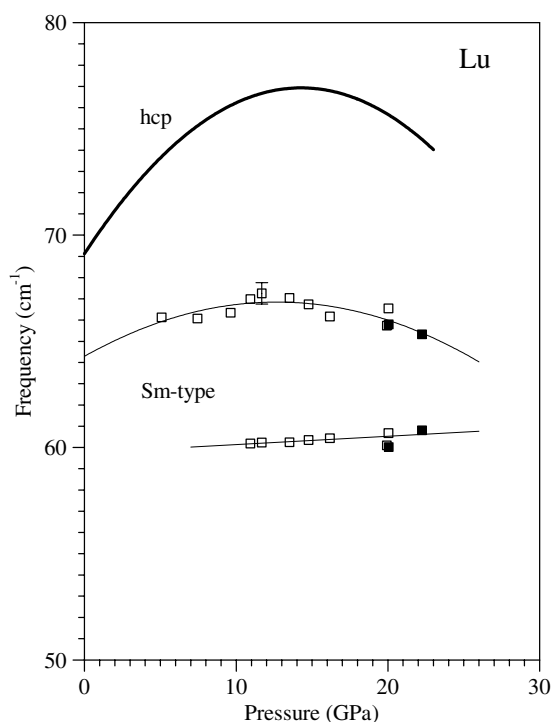


**Figure 5.** Raman spectra of various phases of Lu. Upward arrows indicate pressure increase and downward arrows indicate pressure decrease.

of acoustic phonons which drive the phase transitions in bcc- and fcc-Cs; in particular, a lowering in frequencies of the whole phonon spectrum has been predicted in association with the transition to Cs-III [34]. Indeed, unusual behaviour was found in a recent investigation up to 4 GPa of the longitudinal acoustic (LA)  $q = (100)$  phonons using inelastic x-ray scattering, which shows up in a markedly sublinear pressure shift in the bcc phase near the transition to fcc, while it is nearly pressure independent in the fcc phase [35]. Clearly, theoretical lattice-dynamical studies, which explicitly investigate the effect of the electronic structure and its pressure-induced changes on the mode frequencies, are necessary to understand the lanthanides' anomalies from a microscopic point of view.

The regular structures of the rare-earth metals can be considered as different stacking sequences of close-packed hexagonal layers: AB for hcp, ABABCBCAC for Sm-type, ABAC for dhcp, and ABC for fcc. The net result of any of these transitions is a displacement of certain hexagonal layers by an amount  $a/3$  perpendicular to the  $c$ -axis. The  $E_{2g}$  mode is a shear mode, in which these hexagonal planes are vibrating against each other perpendicular to the  $c$ -axes. It is reasonable to assume that the rearrangement of the stacking sequence may require the weakening of certain interlayer force constants, which should manifest itself in the observed frequency anomalies. In this simple picture one might expect similar anomalies to occur in general for such phase transitions and not to be a consequence of the special electronic structure of the lanthanides. In this respect comparisons with hcp  $\rightarrow$  fcc transitions in solids with different electronic structure might be helpful, since the structural sequence in the lanthanides can also be considered as an hcp  $\rightarrow$  fcc transition proceeding stepwise via the Sm-type and dhcp structures. In Co the entire TA branch goes down in energy and  $C_{44}$  sharply decreases—which is equivalent to a decrease of the  $E_{2g}$  mode frequency—when the

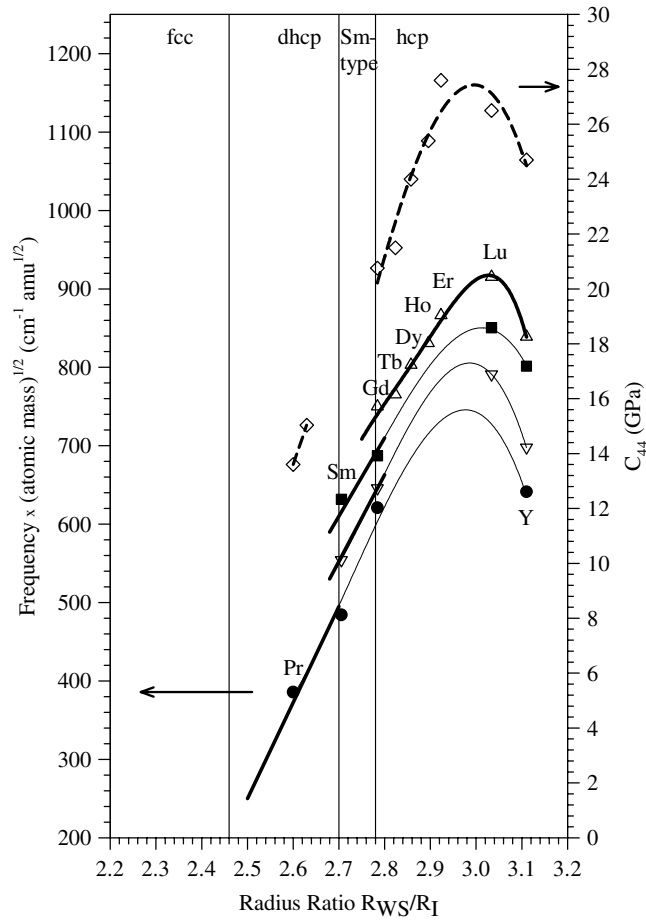




**Figure 6.** Pressure shift of Raman modes in various phases of Lu. Thick solid curve: hcp [4]; thin solid curve: Sm-type; solid symbols: loading; open symbols: unloading. The lines serve as guides for the eye.

transition from hcp to fcc around 700 K is approached [36]. While this behaviour is very similar to that in the regular lanthanides, no anomalies have been reported for the acoustic branches and for  $C_{44}$  near the transitions from hcp to dhcp and from dhcp to fcc in the similar system Co 0.85% Fe [37]. Co exhibits also an hcp  $\rightarrow$  fcc transition in the pressure range 105–150 GPa [38]. Though the  $E_{2g}$  mode does not soften in the pressure range close to the transition to fcc, a gradual reduction in the pressure dependence of the  $E_{2g}$  mode—connected with a comparably low mode Grüneisen parameter—and of  $C_{44}$  has been observed [39]. This anomalous behaviour has been attributed to the magnetic–nonmagnetic nature of the hcp  $\rightarrow$  fcc pressure-driven transition in Co [39]. The non-occurrence of  $E_{2g}$  softening might be connected with the hcp  $\rightarrow$  fcc transition in Co being of reordering martensitic type for which, in contrast to displacive type transitions, no softening should occur [40]. It appears then that softening of the  $E_{2g}$  mode and of  $C_{44}$  are not generally associated with hcp  $\rightarrow$  fcc transitions. On the other hand, the pressure-induced hcp  $\rightarrow$  fcc transitions, studied so far, exhibit at least low  $E_{2g}$  mode Grüneisen parameters as less marked precursor effects.

It is now widely accepted that the initial structural sequence of the regular lanthanides can be attributed to s–d transfer. The 4f-electrons are believed to be localized at each atom with very little involvement in the chemical bonds. At higher pressures, however, the narrow 4f-bands overlap more and their interatomic interactions increase, finally leading to 4f-delocalization, which is associated with the appearance of low-symmetry structures like the  $\alpha$ -uranium type lattice. One may ask to what extent 4f-electrons already contribute to other bonding-dependent properties in the s–d transfer dominated parts of the lanthanides’ phase diagrams, in particular in regions close to the delocalization regime. In this respect the present data provide quite stringent constraints—phonon frequencies derive from the second derivative of the total energy with respect to atomic displacements—for future computational attempts, which investigate if



**Figure 7.** Scaled frequencies (present study, [4, 6, 7, 21–23]) and elastic moduli  $C_{44}$  [26–28] of regular lanthanides at normal conditions versus radius ratio  $R_{WS}/R_I$ . Ionic radii from [29]. Scaled frequencies: open triangles upward—hcp; full squares and open triangles downward—Sm-type; full circles—dhcp. Elastic constant  $C_{44}$ —open diamonds. The solid (frequencies) and dashed ( $C_{44}$ ) curves connecting the data points serve as guides for the eye.

4f-electron contributions are necessary to accurately reproduce the pressure dependence of the experimental frequencies for the lanthanides with occupied 4f-shells; in doing so the accuracy of those calculations disregarding 4f-electrons can be determined by a comparison with the data for Y, where no f-electrons are present.

## 5. Conclusions

The present study reveals common trends in the lattice dynamics and elasticity of the regular lanthanides: a softening of the transverse optical and related acoustic modes as well as of the elastic shear modulus  $C_{44}$  throughout the entire structural sequence hcp  $\rightarrow$  Sm-type  $\rightarrow$  dhcp  $\rightarrow$  fcc, both under pressure for the individual metals and also at normal conditions along the lanthanide series. Similar anomalies have also been observed in part in other hcp metals, and an understanding from a microscopic point of view seems

to be of more general interest. In particular, theoretical investigations would be helpful in elucidating the possible effects of the pressure-induced changes in the electronic structure of the lanthanides on the pressure response of lattice vibrations. Since the magnitude of the phonon frequencies is derived from the second derivative of the lattice energy with respect to long-wavelength atomic displacements, the results of the present study represent a highly sensitive data set for testing the adequacy and accuracy of such calculations.

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