Lattice Vibrations and Electronic Transitions in the Rare-Earth Metals: Praseodymium under Pressure

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Praseodymium was investigated by Raman spectroscopy under pressure. A negative pressure shift of the E_{2g} mode is observed in the dhcp phase, which indicates that the initial structural sequence hcp → Sm-type → dhcp → fcc as a whole in the regular lanthanides is associated with a softening of this mode. The pressure response of the phonon modes, observed in the monoclinic and α-uranium phases, where $4f$ bonding becomes important, is characteristic for anisotropic bonding properties.

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The regular trivalent lanthanides are dominated by two electronic effects, which are the driving forces responsible for their structural behavior. First, *s-d* transfer dominates the initial structural sequence hcp → Sm-type → dhcp → fcc → distorted fcc [1]. A second electronic anomaly involves $4f$-electron delocalization, which is associated with the destabilization of the highly symmetric, low-pressure structures and the appearance of highly asymmetric structures like the α-uranium type lattice [2].

The phonon frequencies are determined by the interatomic forces, which in metals are intimately linked to the electronic structure. The pressure tuning of the electronic band structure and, in particular, electronic transitions affect the lattice vibrational properties and as a consequence also elasticity and many thermal parameters, which are related to, or determined by, phonons.

Previous high-pressure studies of lattice vibrations in the lanthanides have revealed common trends for the transitions from hcp to the Sm-type structure, which are associated with a softening of the E_{2g} mode [3] and of the elastic shear modulus C_{44} [4]. No high-pressure data of phonons are available for the lanthanides in the further course of *s-d* transfer and in the regime where f-electron bonding becomes important.

For metals, lattice-dynamical properties are usually calculated by methods based on density functional theory (DFT) and frequencies, obtained for highly symmetric lattices over a broad pressure range, typically agree within 5% to 10% with the room temperature experimental values [5–9]. Inclusion of thermal effects [10–12], which are usually not contained in these calculations, can result in a disagreement between experiment and theory by 20%. For rare-earth metals under pressure, theoretical studies of phonons are not available at present. Recently it has been pointed out that DFT does not work properly for the region of f-electron delocalization [13,14]. Therefore it is unclear, if such calculations can correctly predict the lattice dynamics of the lanthanides at high pressures.

Such results demonstrate that the present knowledge of the lattice dynamics of the lanthanides is incomplete and far from being understood. To proceed a step further in this subject, we have studied Pr, which is an excellent candidate for this purpose: Pr crystallizes in the dhcp structure at ambient conditions and passes through the remaining part of the close-packed structural sequence with increasing pressure [15–18]; a transition to the α-uranium structure occurs around 20 GPa and is associated with a volume collapse of approximately 17%, which suggests that the f-shell delocalization occurs in a discontinuous manner in Pr [15–18]. In recent studies, a monoclinic ($C2/m$) phase has been observed prior to the formation of the α-uranium phase in the lanthanides [18–20] and was found to be stable in Pr around 12 GPa [18].

The results for lanthanides are also helpful in understanding the lattice dynamics of systems like the actinides under pressure, where similar electronic effects are important [1]. Since phonon frequencies are derived from the second volume derivative of the lattice energy, in general they represent a highly sensitive data set for testing the adequacy and accuracy of computational methods.

High pressures were generated in a diamond anvil cell. Polycrystalline Pr samples (kindly provided by W. B. Holzapfel) were loaded under oil in order to prevent oxidation. No pressure medium was utilized since Pr is extremely soft. The 514.5 nm line of an Ar^+ laser was used to excite the Raman spectra. The scattered light was analyzed using a triple spectrograph equipped with a liquid-nitrogen-cooled charge-coupled device multichannel detector. The E_{2g} phonon of Zn [7] was used as an internal pressure marker. The frequency uncertainty is 0.3 cm^{-1} and the pressure uncertainties range from 0.05 GPa below 10 GPa to 0.5 GPa at higher pressures, where they mainly originate from slight pressure relaxations during data collection.

Raman spectra of Pr metal at various pressures are shown in Fig. 1. Up to 7 GPa, one low-frequency mode around 30 cm^{-1} with a negative pressure shift is observed.

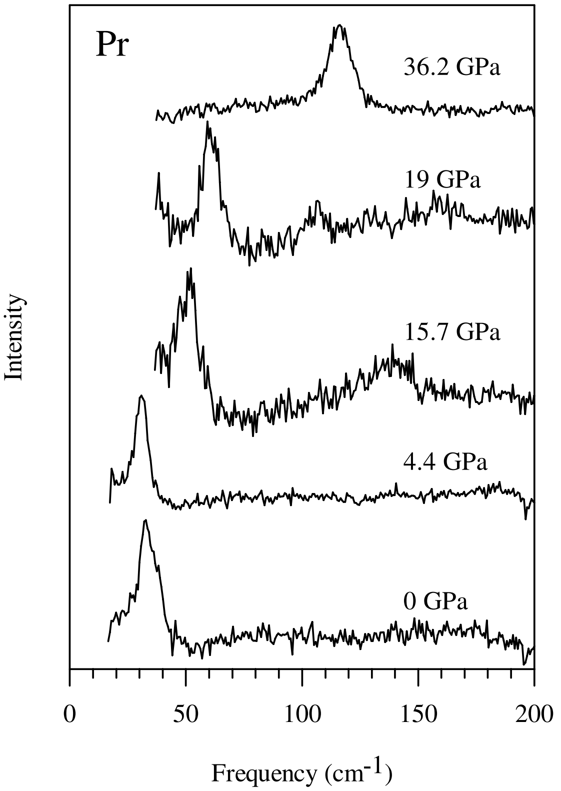

FIG. 1. Raman spectra of Pr in various phases: dhcp (0 and 4.4 GPa), monoclinic phase (15.7 GPa), phase mixture of monoclinic and α uranium (19 GPa), and α uranium (36.2 GPa).

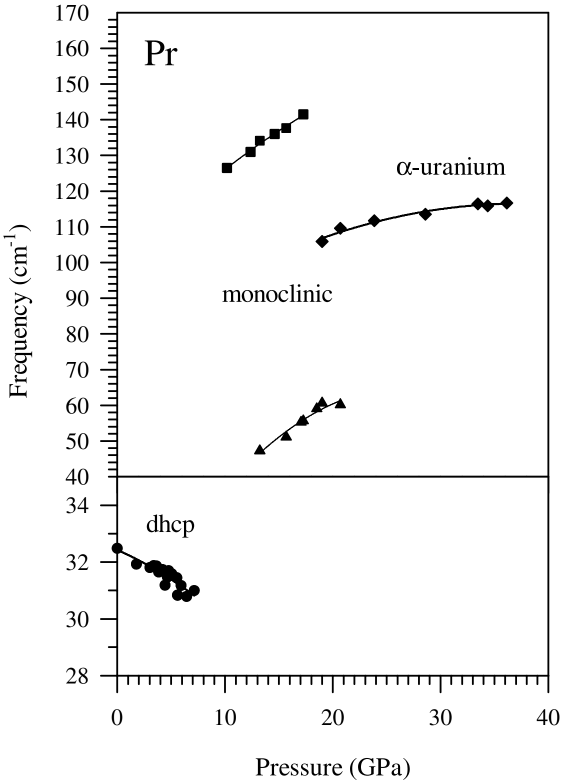

FIG. 2. Pressure shift of Raman modes in various phases of Pr.

Between 7 and 10 GPa no Raman modes could be detected. Above 10 GPa two new peaks with frequencies around 125 cm^{-1} and 50 cm^{-1} appeared. These peaks vanish at 20 GPa, where one mode around 105 cm^{-1} appeared, which could be observed to the maximum pressure of the experiments. The peaks above 10 GPa exhibit a positive pressure shift as shown in Fig. 2. The average mode Grüneisen parameters were determined by fitting the $\ln\nu_i$- $\ln V$ data to a first order polynomial and are summarized in Table I. The *V-P* data were taken from Ref. [16].

The crystallographic data of the various phases and the Raman-active modes are summarized in Table II. The dhcp phase has one Raman-active mode, the fcc lattice with one atom per primitive unit cell has no optical modes and hence no Raman signals are expected in the stability field of this phase. No clear assignment has been made up to now for the distorted-fcc structure for which several structures have been suggested [21–23]. Three Raman-active modes are expected both in the monoclinic and in the α-uranium phase.

In x-ray diffraction studies [15–18] the dhcp → fcc transition has been observed at 4 GPa and the onset of the fcc distortion around 7 GPa. In the present study the E_{2g} mode of the dhcp phase could be observed up to 7 GPa. Above 5 GPa the intensity of the E_{2g} mode decreased due to increasing portions of the fcc phase, which is an indication of the well-known sluggishness of this transition. Between 7 and 10 GPa no Raman signals could be observed in agreement with the fcc phase exhibiting no Raman-active modes. Two modes have been observed between 10 and 20 GPa, the pressure range in which the monoclinic phase has been observed [18]. The band above 20 GPa is characteristic for the α-uranium phase. Not all three modes for the monoclinic and the α-uranium phase were observed, which might be due to low intensities of these modes, for example, as a result of preferred orientation, which is not unusual in high-pressure studies. In α uranium, the frequencies of the three optical modes are close together with 82, 104, and 120 cm^{-1} at ambient conditions [24]. Assuming the observed band in Pr to be composed of three modes would mean a smaller frequency separation for Pr than in uranium, which was not resolved in the present experiments.

TABLE I. Average mode Grüneisen parameters γ_{ave} for the observed vibrational modes of various phases of Pr.

Phase	Mode	γ_{ave}
dhcp	33 cm^{-1}	−0.25
monoclinic	50 cm^{-1}	2.3
	120 cm^{-1}	0.87
α uranium	110 cm^{-1}	0.82

TABLE II. Crystallographic data and Raman-active modes for zero wave vector of various phases of Pr.

Phase	space group	atoms per primitive unit cell	site symmetry	Raman-active modes
dhcp	$D_{6h}^4(P6_3/mmc)$	4	D_{3h}	E_{2g}
monclinic	$C_{2h}^3(C2/m)$	2	C_2	$1A_g + 2B_g$
α uranium	$D_{2h}^{17}(Cmcm)$	2	C_{2v}	$A_g + B_{1g} + B_{2g}$

The E_{2g} mode exhibits a negative pressure shift throughout the whole stability field of the dhcp phase. The frequency of this mode also decreases in the hcp phase of the regular lanthanides when the transition to Sm-type is approached and preliminary results indicate that it continues to decrease in the Sm-type phase [3]. This means that the whole initial sequence hcp → Sm-type → dhcp → fcc in the regular lanthanides is associated with E_{2g} mode softening. These close-packed structures differ only in the stacking sequence of their hexagonal layers. The rearrangement of the stacking sequence in these phase transitions might require weakening of some interlayer bonds, which leads to softening of the E_{2g} mode, since the interlayer bonds are just probed by this mode [25]. Within this simple picture one would expect similar anomalies to occur in transitions between these structures in general. In this respect comparison with hcp-fcc transitions in other solids might be helpful, since the initial sequence in the lanthanides can also be considered as a hcp → fcc transition proceeding stepwise via the Sm-type and dhcp structures. For hcp-Co the elastic modulus C_{44} shows a drop in the vicinity of the transition to fcc around 700 K [26]. Since for hexagonal metals the E_{2g} mode is intimately linked to the macroscopic elastic shear modulus C_{44}, $\nu(E_{2g})^2 \propto C_{44}$, these results for C_{44} imply a decrease of the E_{2g} mode frequency in association with the hcp → fcc transition [4]. While this behavior resembles much the situation in the lanthanides, the case of the similar system Co–0.85%Fe, for which no C_{44} anomalies have been reported [27], as well as the absence of E_{2g} mode softening in the high-pressure hcp → fcc transition in Co [28] seem to thwart a generalized behavior of the E_{2g} mode in these transitions.

From a thermodynamic point of view the special electronic properties of the lanthanides may have important impacts on the pressure response of the lattice vibrations since s-d electron transfer is known to be responsible for softening of the equation of state and for a low lattice Grüneisen parameter in the low-pressure phases of the lanthanides [29]. Not only optical modes but also acoustic phonons exhibit negative frequency shifts and contribute to the low lattice Grüneisen parameter, because a lowering of C_{44} is equivalent to a decrease of the slope of the transverse acoustic (TA) branch. This has been noticed also from ultrasonic studies for Pr, where the decrease of long-wave transverse and longitudinal acoustic phonons in association with the transitions to fcc and distorted-fcc has been attributed to special aspects of $s - d$ transfer [30].

The two modes, observed for the monoclinic phase, exhibit quite different values for the mode Grüneisen parameter (see Table I), which is characteristic for anisotropic materials. In such solids the various vibrational modes are controlled by bonds, which respond differently under compression. Indications for anisotropy can be deduced from the axial ratios, $c/a = 0.94$ and $b/a = 0.53$ for Pr at 15 GPa, which have to be compared with the ideal values 1.0 and 0.577, respectively. The mode observed in the α-uranium phase has a comparably low Grüneisen parameter like the higher frequency mode of the monoclinic phase. Such low values can signal mode softening, for example, in connection with a phase transition, but they can also result from anisotropic bonding properties, for example, as in Be [31]. Since Pr is known to remain stable in the α-uranium phase up to at least 103 GPa [18], the low γ value gives another indication of anisotropic bonding originating from f-electron contributions, which become important in this part of the phase diagram.

In this respect, the present data represent important constraints for the results of future attempts to describe quantitatively the lattice dynamics from first principles in the regime of the rare-earth metals, where f electrons take part in bonding. In the pressure range that is dominated by d electrons, the present study of Pr, together with previous data, shows that softening of the E_{2g} mode is involved in the transition from hcp to fcc via Sm-type and dhcp in the regular lanthanides. There is evidence that this anomaly is not restricted to lanthanides but that it occurs also for hcp → fcc transitions in other metals.

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