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

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Introduction

The structural behaviour of the regular trivalent lanthanides is governed by two electronic effects: first of all, s-d transfer, which dominates the initial structural sequence hcp \rightarrow Sm-type \rightarrow dhcp \rightarrow fcc \rightarrow distorted fcc, observed for the individual metals under pressure as well as along the lanthanide series with decreasing atomic number at normal pressure, and secondly 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 [Johansson & Brooks 1993, Holzapfel & Benedict 1993, Söderlind 2002].

Pr, a regular lanthanide, crystallizes in the dhcp structure at ambient conditions, passes through the remaining part of the closed-packed structural sequence with increasing pressure, transforms around 12 GPa to a monoclinic (C2/m) lattice and around 20 GPa to the α -uranium structure, which is associated with a volume collapse of approximately 17% suggesting that the f-shell delocalization occurs in a discontinuous manner in Pr [Endo et al. 1977, Grosshans et al. 1982, 1983, Chestnut & Vohra 2000, Dmitriev et al. 2004].

While the structural behaviour of Pr under pressure appears to be rather well investigated and understood over a broad pressure range, this is not the case for its lattice dynamical behaviour. Here we report on Raman spectroscopic studies of Pr up to 40 GPa, i.e., in a pressure range in which both electronic transitions occur.

The phonon frequencies are determined by the interatomic forces, which in metals are intimately linked to the electronic structure. One can expect that 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. 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 [Johansson & Brooks 1993]. Since frequencies of optical zone centre modes derive from the second derivative of the lattice energy with respect to long-wavelength atomic displacements, they represent a highly sensitive data set for testing the adequacy and accuracy of computational methods. 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 [Althoff et al. 1993, Ostanin et al. 1998, Vocadlo et al. 2000, Olijnyk et al. 2000, 2001]. Inclusion of thermal effects [Grant et al. 1973, Baptizmanskii et al. 1979, Ponosov & Bolotin 1985, 1993, Bolotin et al. 2001, Mogilenskikh et al. 2003], 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 delocalisation [Lundin et al. 2000, Savrasov et al. 2001]. Therefore it is unclear, if such calculations can correctly predict the lattice dynamics of the lanthanides at high pressures.

Experiment

Raman studies were made on polycrystalline Pr samples, which were loaded under oil into a high-pressure diamond-anvil cell (DAC) in order to prevent oxidation. Raman spectra were excited with the 514.5 nm line of an Ar⁺ laser focused down to $\approx 10 \ \mu\text{m}$. Scattered light was analyzed at an angle of 135° with respect to the incoming laser beam using a 0.6 m triple spectrograph and a liquid-nitrogen-cooled CCD multichannel detector. No pressure medium was utilized since Pr is extremely soft. The E_{2g} phonon of Zn [Olijnyk et al. 2000] was used as 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.

Results

Raman spectra of Pr metal at various pressures are shown in Fig. 1. Up to 7 GPa, one lowfrequency mode around 30 cm⁻¹ with a negative pressure shift is observed. Between 7 GPa 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 vanished 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 $\ln n_i - \ln V$ data to a first order polynomial and are summarized in Table 1. The *V-P* data were taken from Grosshans et al. (1983).

Phase	Mode	Yave
dhcp	33 cm ⁻¹	-0.25
monoclinic	50 cm ⁻¹	2.3
	120 cm ⁻¹	0.87
a-uranium	110 cm ⁻¹	0.82

TABLE 1. Average mode Grüneisen parameters γ_{ave} for the observed vibrational modes of various phases of Pr.



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



The dhcp lattice, space group D_{6h}^4 (*P6₃/mmc*) has four atoms per unit cell on sites of symmetry D_{3h} and one mode, the double degenerate E_{2g} mode, shows Raman activity. 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 [Vohra et al. 1984, Smith & Akella 1984, Hamaya et al. 1993]. In the monoclinic lattice, space group C_{2h}^3 (*C2/m*) with 2 atoms on sites of symmetry C_2 , 3 modes, $1A_g + 2B_g$, are Raman active. The α -uranium phase has space group D_{2h}^{17} (*Cmcm*) and the 3 Raman active modes $A_g + B_{1g}$ + B_{2g} derive from the 2 atoms on sites of symmetry C_{2v} .

In x-ray diffraction studies [Endo et al. 1977, Grosshans et al. 1982, 1983, Chestnut & Vohra 2000, Dmitriev et al. 2004] the dhcp \rightarrow 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 transion. Between 7 GPa 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 GPa and 20 GPa, the pressure range in which the monoclinic phase has been observed [Chestnut & Vohra 2000, Dmitriev et al. 2004]. 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 cm⁻¹, 104 cm⁻¹ and 120 cm⁻¹ at ambient conditions [Crummett et al. 1979]. 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.

Discussion

The E_{2g} mode of dhcp-Pr exhibits a negative pressure shift throughout the whole stability field of the dhcp phase, a behaviour observed also in other regular lanthanides. A frequency decrease of this mode occurs also in the hcp phase of the regular lanthanides, when the transition to Sm-type is approached, and in the Sm-type phase [Olijnyk 1994, 2005, Olijnyk et al. 2004, Olijnyk & Jephcoat 2005]. This means that the whole initial sequence hcp \rightarrow Smtype \rightarrow dhcp \rightarrow fcc in the regular lanthanides is associated with E_{2g} mode softening. In hexagonal metals the E_{2g} mode is intimately linked to the macroscopic elastic shear modulus C_{44} , $v(E_{2g})^2 \propto C_{44}$, implying a weakening of elastic modulus C_{44} in connection with these phase transitions [Olijnyk & Jephcoat 2000a]. Simultaneously with these optical modes also acoustic phonons exhibit negative frequency shifts, because a lowering of C_{44} is equivalent to a decrease of the slope of the transverse acoustic (TA) branch. 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 dist. fcc phase transitions and has been related to special aspects of the s-d transfer [Boguslavskii et al. 1989].

On constructing their generalized phase diagram for the regular lanthanides, Johannson & Rosengren (1975) have introduced the ratio of the Wigner-Seitz radius R_{WS} to the ionic radius R_1 (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 for the individual metals 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 Fig.3 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 like for the individual members under pressure, i.e., mode softening as well as weakening of C_{44} occur also along the lanthanide series.

A qualitative explanation for this unusual pressure shift can be obtained by considering the close-packed structures involved in the phase transitions, which differ only in the stacking sequence of the hexagonal layers, ABAB for hcp, ABABCBCAC for Sm-type, ABAC for dhcp and ABC for fcc. In these phase transitions regrouping of hexagonal layers may require weakening of some of the force constants responsible for bonding between successive hexagonal planes, which manifests itself in the observed mode softening, since these modes correspond to vibrations of successive hexagonal planes against each other perpendicular to the *c*-axes, which probe the resistance against shearing of these planes. 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 \rightarrow fcc transition proceeding stepwise via the Sm-type and dhcp structures. For hcp-Co the elastic shear modulus C₄₄ shows a drop in the vicinity of the transition to fcc around 700 K [Strauss et al. 1996], which is equivalent to a decrease of the E_{2g} mode frequency. While this behaviour resembles much the situation observed in the lanthanides, the case of the similar system Co-0.85%Fe, for which no C₄₄ anomalies have been reported in association with the temperature-induced transitions from hcp to dhcp and from dhcp to fcc [Prem et al. 1999], as well as the absence of E_{2g} mode softening in the high-pressure hcp \rightarrow fcc transition in Co [Goncharov et al. 2004] do not support the view that softening of these modes occurs in general as precursor effect for these phase transitions.



Fig. 3: Scaled frequencies and elastic moduli C₄₄ of regular lanthanides at normal conditions versus radius ratio R_{VS}/R₁ [Olijnyk 2005]. Scaled frequencies: open triangles upward-hcp; full squares and open triangles downward-Sm-type; full circles-dhcp. Elastic constant C₄₄-open diamonds. The solid (frequencies) and dashed (C₄₄) lines connecting the data points serve as a guide for the eye.

The low-pressure phases of the regular rare earth metals in general are characterized by very low lattice Grüneisen parameters, which has been attributed to the electronic s-d transition softening [McMahan et al. 1981]. The optical modes and the related acoustic branches with their low and negative mode Grüneisen parameters contribute to these low lattice Grüneisen parameters, which 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. 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 these anomalies from a microscopic point of view.

The two modes, observed for the monoclinic phase, exhibit quite different values for the mode Grüneisen parameter (see Table 1), 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 [Chestnut & Vohra 2000]. 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 [Olijnyk & Jephcoat 2000b]. Since Pr is known to remain stable in the α -uranium phase up to at least 103 GPa [Chestnut & Vohra 2000], 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.

Conclusion

The frequency shifts of the observed Raman mode in the dhcp phase of Pr shows the same qualitative behaviour under pressure as in other regular lanthanides indicating common trends in their lattice dynamics, that is, the whole structural sequence hcp \rightarrow Sm-type \rightarrow dhcp \rightarrow fcc involves softening of optical and acoustic modes implying also anomalies in their elastic behaviour. Similar anomalies have been observed in part also in other hexagonal metals and an understanding from a microscopic point of view seems to be of more general interest. The pressure response of the phonon modes, observed in the monoclinic and *a*-uranium phases, where 4f-electrons take part in bonding, is characteristic for anisotropic bonding properties.

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