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ON STRUCTURAL SYSTEMATICS OF THE LANTHANIDES UNDER PRESSURE

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Résumé - Pour tous les lanthanides trivalents réguliers, on a observé sous pression jusqu'à 40 GPa la séquence suivante de structures cristallines : hcp - structure type Sm - dhcp - fcc - fcc distordue. De plus, on a prouvé une délocalisation des électrons f non seulement dans le praséodyme mais également dans le néodyme et le samarium. Les résultats pour l'europlum et l'ytterbium sont discutés en envisageant l'existence d'un état de valence intermédiaire.

Abstract - The crystal structure sequence hcp - Sm type - dhcp - fcc - dist. fcc has been observed for all the regular trivalent lanthanides under pressures up to 40 GPa. In addition, evidence for a delocalization of the f electrons is observed not only in praseodymium, but also in neodymium and samarium. The data for europium and ytterbium are discussed with respect to a possible mixed valent state.

INTRODUCTION

The lanthanide metals scandium (Sc), yttrium (Y) and lanthanum (La) to lutecium (Lu) are all trivalent in the metallic state at ambient conditions with the exception of divalent europium (Eu) and ytterbium (Yb). The rare earth crystal structure sequence fcc - dhcp - Sm type - hcp is observed across the lanthanide series with increasing atomic number. It was realized in earlier high pressure studies (1-4) that the rare earth crystal structure sequence also appears in individual elements by the application of pressure. Duthie and Pettifor (5) related the pressure induced structural sequence to the increase of the d band occupancy N_d from an $sp - d$ transfer under pressure. Furthermore, Johansson and Rosengren (6) predicted a transition towards the trivalent state for Eu and Yb. The present studies were intended to collect further experimental support for these general ideas.

EXPERIMENTAL

The lanthanide elements with the exception of cerium and promethium were investigated to 40 GPa and above in a gasketed diamond anvil cell by energy dispersive X-ray diffraction with synchrotron radiation. The details of the experimental techniques are given elsewhere (7). The use of nitrogen as pressure transmitting medium leads to nearly hydrostatic conditions over the whole pressure range. The Ruby R_1 -fluorescence method was used for pressure determination with the calibration constant of 365 pm/GPa (8).

THE REGULAR LANTHANIDES

Experimental evidence for the regular rare earth crystal structure sequence has already been reported for various lanthanides in the lower pressure region (9,10). The present studies on the regular trivalent rare earth metals Y, La, Pr, Nd, Sm, Gd, Td, Dy, Ho, Er, Tm and Lu confirm the structural sequence hcp - Sm type - dhcp - fcc - dist. fcc for all these elements in the available pressure range (11,12). Y, Gd and Tb undergo the whole series of transitions from hcp to dist. fcc. All these elements show a smooth behaviour in their P-V data without any noticed volume change at the phase transitions (cf. fig.1 for e.g. Gd). The occurrence of the second order phase transition from fcc to dist. fcc (13), the ultimate high

pressure phase of the regular lanthanides, is due to a gradual distortion of the fcc lattice and can be related to soft phonon modes near the L point in the Brillouin zone (13-15). Vohra et al. (16) assigned the rhombohedral space group $P3_21$ to this distorted cubic lattice. Finally, it should be mentioned, that the results on Y support the view that no bonding contribution from f electrons is required for the stabilization of the regular rare earths crystal structures.

f BONDING IN RARE EARTH METALS

The special properties of Ce (17) and the light actinides are generally attributed to delocalized f electrons. Furthermore, it is recognized that the application of pressure to light lanthanides (Ce, Pr,...) and heavy actinides (Am, Cm,...) can force the localized f^n configuration to participate in bonding which leads to the appearance of low symmetry crystal structures. A typical light actinide crystal structure (α -uranium) has been identified experimentally in Ce between 5 GPa and 13 GPa (18). 4f delocalization was also reported for Pr (19), where a new phase above 20 GPa was indexed as hexagonal. More recently (20,21), however, this structure was identified as α -uranium. The P-V relationship of Pr is shown in fig.1 together with data for Gd for comparison. The delocalization is accompanied by a volume collapse of about 9.3% and a steep increase of the bulk modulus.

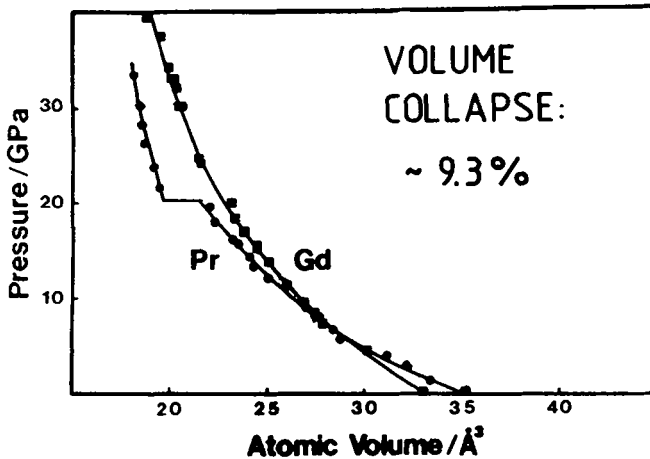


Fig.1: Volume vs. pressure for praseodymium and gadolinium at room temperature. The volume collapse at the transition from dfcc to α -U in Pr is about 9.3%

In the present investigation, a new high pressure structure was found in Nd and Sm. The transition pressures are 41(1) GPa for Nd, but only 33(4) GPa for Sm. The nature of this new phase is not yet clear, but the symmetry seems to be orthorhombic or even lower. The decrease in the transition pressure from Nd to Sm stimulated similar experiments on Gd and Tb, but no change in crystal structures from dist. fcc occurred in Gd up to 47 GPa and in Tb up to 40 GPa. It should be noted, that the occurrence of low symmetry crystal structures in Pr and most probably in Nd and Sm fits into the systematics of rare

earths, where such structures appears under pressure at a critical amount of f bonding, though the relative low transition pressure in Sm needs some further theoretical considerations.

DIVALENT Eu AND Yb

A different behaviour is observed in the rare earth elements Eu and Yb (9), which are close to the divalent state under ambient conditions. At higher pressures, these elements were expected to exhibit normal trivalent behaviour with the regular structural sequence (6). The observed sequences are however

fcc $\xrightarrow{4\text{GPa}}$ bcc $\xrightarrow{35\text{GPa}}$ hcp for Yb (22-24) and bcc $\xrightarrow{12.5\text{GPa}}$ hcp $\xrightarrow{32\text{GPa}}$ Eu III for Eu (23, 24). The hcp-like phase of Eu III has been reported by Takemura et al. (25) to occur already at 18 GPa, whereas the present study found evidence for this structure only above 32 GPa.

A comparison of Eu and Yb with its neighbours Gd and Lu points to a continuous approach towards the trivalent state as indicated also by L_{III} edge absorption studies on Yb (26). However, the occurrence of this new phase in Eu may indicate, that europium shows either an intermediate valence over a wide range of pressures or even more complex behaviour.

SCANDIUM

The 3d metal Sc does not undergo the regular rare earth structural sequence. Sc transforms in a sluggish transition between 20 GPa and 26 GPa from hcp to tetragonal β -Np structure (27) without any further transition up to 40 GPa. This difference between Sc and Y indicates that simple canonical band theory calculations cannot explain this structural sequence in detail.

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