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Structural Studies on Dy to 119 GPa and Applications to Lanthanide Systematics

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Abstract

The Rare Earth elements (REE) are known to undergo crystallographic as well as electronic structure changes with applied pressure. On increasing pressure, the trivalent lanthanides follow the sequence hcp → Sm-type → dhcp → fcc → dfcc. In this report we present room-temperature high-pressure x-ray diffraction data for Dy as well as our observations on the post-dfcc phases and concomitant volume changes in the heavy REE.

Introduction

The structural systematics of the Lanthanides have previously been studied in detail (Jayaraman 1978, Holzapfel 1995, Akella 1995). With increasing pressure (or decreasing atomic number) the trivalent Lanthanides undergo the structural sequence hcp → Sm-type → dhcp → fcc. At even higher pressures, several lighter Lanthanides transform to a distorted-fcc (dfcc) structure. Experiments on Pr (Hamaya, 1994) indexed this structure as hR24, a hexagonal representation of space group R-3m with Z=24. An additional study of this particular phase transition (Porsch, 1994) suggests a lack of evidence for a first-order transformation. The change from dhcp → hR24 would be a weakly first-order transformation, and Porsch et al. propose Cmmm as a structural candidate allowing a pure second-order phase transition. The dfcc phase has been observed in Pr as well as Nd, Sm, Gd, and Dy. Only Pr and Dy have been specifically indexed as hR24, the others were indexed either as six layered hexagonal or simply as superlattice reflections of fcc.

Following the dfcc phase, lower symmetry phases such as orthorhombic a-U or monoclinic (C2/m or bcm) have been observed (Baer 2003, Chesnut 2000, Hua 1998). The lowering of symmetry is generally attributed to the participation of the 4f-electrons in bonding resulting from pressure-induced delocalization (Johansson 1974). The association of observed volume changes with f-electron delocalization tends to be less predictable. For example, Pr exhibits a monoclinic phase prior to the volume collapse, while no noticeable volume change is observed for Nd or Sm under compression. Alternatively, the volume collapse in Ce is isostructural and also occurs prior to the low symmetry monoclinic phase.

For the heavier Lanthanides, the lower pressure phases follow the same structural sequence as the lighter Lanthanides through the dhcp phase (Grosshans, 1992). A pristine fcc phase is observed in Tb, but not in any heavier Lanthanides. Instead, Dy, Ho, Er (Akella, 1995), and Lu (Chesnut, 1998) transform directly into dfcc, as shown in Table 1. In addition, few experiments exist detailing the post-dfcc phases of the heavier Lanthanides.

Experimental Results

We have recently performed *in situ* x-ray diffraction studies on Dy to 119 GPa (Patterson, 2004), as well as Ho and Tm. X-ray spectra were collected on beamline X-17C at the National Synchrotron Light Source, Brookhaven National Laboratory, and at HP-CAT at the Advanced Photon Source, Argonne National Laboratory. Samples from the Materials Preparation Center, Ames Laboratory of at least 99.9% purity were loaded into a Mao-Bell type diamond anvil cell along with either Cu or Pt as a pressure marker. No pressure transmitting medium was used, and pressures were calibrated against the internal standards using the Vinet (and/or Birch-Murnaghan) EOS with parameters derived from shock data.

Table 1. Structural phase transformations for selected lanthanides. The heavier lanthanides show similar post dhcp-phases, and may be candidates for transformation to a monoclinic phase at higher pressures.

	transition sequence	*reference*
Ce	fcc → fcc' → bcm → bct	Olsen 1985
Pr	dhcp → fcc → hR24 → α-U	Baer 2003
Gd	hcp → Sm-type → dhcp → fcc → dfcc → bcm	Hua 1998
Dy	hcp → Sm-type → dhcp → hR24 → bcm	Patterson 2004
Ho	hcp → Sm-type → dhcp → hR24	current study
Er	hcp → Sm-type → dhcp → dfcc	Akella 1995
Tm	hcp → Sm-type → dhcp → hR24	current study
Lu	hcp → Sm-type → dhcp → hR24	Chesnut 1998

Dy, Ho, and Tm are hcp at ambient conditions, and we observe transformations from hcp → Sm-type → dhcp that are consistent with published values. Fig 1. shows spectra in the dfcc phase for each sample. The suggested Cmmm structure does not fit our data as well as hR24, and since our experimental resolution may not be sufficient to observe the weak first-order nature of the dhcp → hR24 transition, we have indexed each spectrum to hR24 using the atomic positions of Hamaya et al. We do not observe a pure fcc phase for any sample, suggesting that the fcc stability region (if it is non-zero) for these materials may be smaller than our pressure step size. The absence of the fcc phase is also in agreement with earlier measurements (Akella, 1995), supporting the disappearance of the fcc phase from the structural sequence for the heavy Lanthanides.

The transformation from hR24 to body-centered monoclinic (bcm) occurs at 73 GPa in Dy (Patterson, 2004), and is accompanied by a 6% decrease in volume. This transformation is similar to that observed in Gd (Hua, 1998), although the dfcc phase in Gd was indexed as a six-layered hexagonal structure. Preliminary analysis of diffraction spectra of Tm indicates a transformation to a lower symmetry (possibly bcm) structure immediately following the hR24 phase. In the cases of Gd and Dy, the dfcc → bcm transformation is accompanied by a discontinuous change in volume, which is attributed to the delocalization of the 4f-electrons.

In conclusion, our study of Dy, Ho, and Tm to high pressures suggests that there are similarities in the post-dfcc phase transformations for Lanthanides. In our future work, we intend to look in more detail for any possible structural systematics in the high-pressure behavior and concomitant volume changes of heavy REE.

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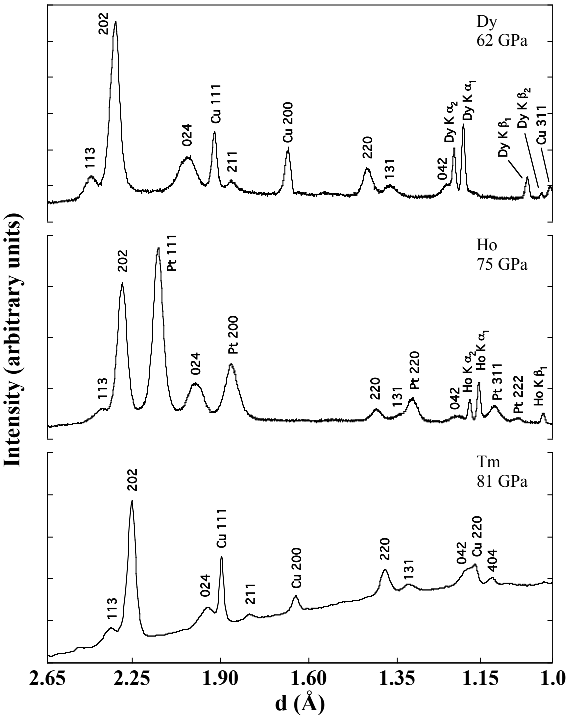

Fig. 1 The dfcc phases for Dy, Ho, and Tm at 62, 75, and 81 GPa respectively. All three phases are consistent with the hR24 structure. The spectra for Dy and Ho are energy dispersive and were collected at NSLS, while the Tm spectrum is angle dispersive and was taken at APS.

References

Akella, J., Smith, G.S., Weir, S.T., Ruddle, C.M., 1995. Ultra-high pressure structural changes study in Dysprosium, Holmium, and Erbium. *In*: W.A. Trzeciakowski, ed. *High Pressure Science and Technology, XV AIRAPT Conference Proceedings*. Warsaw, Poland: World Science, Singapore, 387.

Baer, B.J., Cynn, H., Iota, V., and Yoo, C.-S., 2003. Phase diagram and equation of state of praseodymium at high pressures and temperatures. *Physical Review B*, 67, 134115.

Chesnut, G.N. and Vohra, Y.K., 1998. Phase transformation in lutetium metal at 88 GPa. *Physical Review B*, 57(17), 10221-10223.

Chesnut, G.N. and Vohra, Y.K., 2000. Phase transformations and equation of state of praseodymium metal to 103 GPa. *Physical Review B*, 62(5), 2965-2968.

Grosshans, W.A., Holzapfel, W.B., 1992. Atomic volumes of rare-earth metals under pressures to 40 GPa and above. *Physical Review B*, 45(10), 5171-5178.

Hamaya, N., Sakamoto, Y., Fujihisa, H., Fujii, Y., Takemura, K., Kikegawa, T., and Shimomura, O., 1994. Rietveld Analysis of High-Pressure Phase of Praseodymium. *In:* S.C. Schmidt, et al., eds. *High Pressure Science and Technology, AIP Conference Proceeding No. 309*. New York, NY: AIP, 457.

Holzapfel, W.B., 1995. Structural systematics of 4f and 5f elements under pressure. *Journal of Alloys and Compounds*, 223, 170-173.

Hua, H., Vohra, Y.K., Akella, J., Weir, S.T., and Johansson, B., 1998. Theoretical and experimental studies on gadolinium at ultra high pressure. *Review of High Pressure Science and Technology*, 7, 233-235.

Jayaraman, A., 1978. *In:* K.A. Gschneidner, Jr. and L. Eyring, eds. *Handbook on the Physics and Chemistry of the Rare Earths, Vol 1*. Amsterdam: North-Holland, Ch. 9.

Johansson, B., 1974. The $\alpha-\gamma$ transition in cerium is a Mott transition. *Philosophical Magazine*, 30, 469-482.

Olsen, J.S., Gerward, L., Benedict, U., and Itie, J.-P., 1985. The crystal structure and the equation of state of cerium metal in the pressure range 0-46 GPa. *Physica B*, 133, 129-137.

Patterson, J.R., Saw, C.K., Akella, J., 2004. Static high-pressure structural studies on Dy to 119 GPa. *Journal of Applied Physics*, 95(10), 5443-5446.

Porsch, F. and Holzapfel, W.B., 1994. Symmetry change at the fcc – distorted-fcc phase transition of lanthanides under pressure. *Physical Review B*, 50(22), 16212-16218.

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