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Static High -Pressure Structural Studies on Dy to 119 GPa

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Structural phase transitions in the rare -earth metal Dysprosium have been studied in a Diamond Anvil Cell (DAC) to 119 GPa by x -ray diffraction. Four transformations following this sequence hcp \rightarrow Sm -type \rightarrow dhcp \rightarrow hR24 (hexagonal) \rightarrow bcm (monoclinic) are observed at 6, 15, 43, and 73 GPa respectively. The hexagonal to monoclinic transformation is accompanied by a 6% reduction in volume, which is attributed to delocalization of the 4f electrons, similar to that seen in Ce, Pr, and Gd.

INTRODUCTION

The compression of rare earth metals is known to induce both structural and electron transformations. The trivalent lanthanides (La through Lu excepting Eu and Yb) have been shown to follow a crystal structure sequence with decreasing atomic number or increasing pressure: hcp \rightarrow Sm -type \rightarrow dhcp \rightarrow fcc. ¹ This structural sequence is attributed to the promotion of electrons to the $5s$ -band with increasing pressure. In these pressure regimes, the $4f$ electrons do not contribute to bonding. Further compression studies of the rare earth metals have added a distorted fcc (dfcc) phase to this pressure sequence. ² Still further compression of several rare earth elements has resulted in a transition to a lower symmetry phase, which may be accompanied by a significant volume change. One explanation is that this transition is a Mott

transition,³ in which the electrons become delocalized and now participate in the metallic bond.

Although the delocalization of the electrons is the generally accepted explanation for the collapsed phases, the phase itself depends on the element studied, with at least monoclinic and orthorhombic phases having been observed.

Dy crystallizes in an hcp structure at ambient conditions with $a = 3.5918$ and $c = 5.6518$ Å.⁴ Dy is a trivalent rare earth metal with ambient pressure electronic configuration of (spd)³4f⁹ with 3 electrons in the spd conduction band and 9 electrons in the localized 4f shell. The application of high pressure is expected to cause $\text{d}-\text{d}$ electron transfer in the spd conduction band and at sufficiently high $\text{d}-\text{d}$ pressure cause an eventual delocalization of the 4f shell. Previous studies on Dy have shown it to follow the typical rare earth structural sequence through the fcc phase. Großhans⁵ found pressure induced transformations occurring at about 8, 17, and 43 GPa for the hcp \rightarrow Sm₂-type, Sm₃-type \rightarrow dhcp, and dhcp \rightarrow fcc transitions, respectively. Akella et al.⁶ also observed similar transition pressures, and find the fcc phase to be stable up to 57 GPa. Neither observes a pure fcc phase. In the rare earth metals Pr, Nd, Sm, and Gd, the fcc phase precedes a lower symmetry phase that is associated with electron delocalization. In view of these observations Dy is a good candidate for an fcc \rightarrow 4f shell delocalization transition at pressures greater than 57 GPa. In the present work, we examine the post fcc phases of Dy and the pressure-volume EOS to 119 GPa. Our high pressure studies are motivated by structural transformations in Dy above 57 GPa and the correlation of these transformations to the 4f shell delocalization phenomenon, as well as comparisons with phase changes in neighboring rare earth metals at high compression.

EXPERIMENT

We conducted *in-situ* energy dispersive x-ray diffraction measurements on Dy to 19 GPa. X-ray diffraction spectra were collected on beamline X-17C at the National Synchrotron Light Source of Brookhaven National Laboratory. Typical collimated beam size is on the order of 10 μm by 12 μm from a 2.5 GeV beam. Dy of 99.99% purity was purchased from the Materials Preparation Center at Ames Laboratory. Prior to loading, the sample was scraped and then cleaned with alcohol in order to expose clean metal and reduce the amount of possible oxide. A Mao-Bell type DAC was prepared with type Ia diamonds having a 7.5 $^{\circ}$ bevel from a 300 μm culet to a 50-70 μm central flat. The sample was loaded into a 30-60 μm chamber drilled in a pre-indented tool-steel gasket. Cu was loaded in the sample chamber as a pressure standard, and no pressure medium was employed in order to maximize sample volume and avoid any chemical reactions between the sample and pressure medium. Pressure was calibrated against the internal Cu standard using the Vinet EOS^{7,8},

$$\ln H = \ln K_0 + \eta(1-x) + \beta(1-x)^2 \quad (1)$$

where $H = Px^2 / 3(1-x)$, $\eta = 3/2(\bar{K}_0 - 1)$, and $x = (V/V_0)^{1/3}$. Experimental pressures were calculated using the values $\bar{K}_0 = 143.66$, $\eta = 4.3566$, and $\beta = 13.774$, from the shock data for copper⁹.

RESULTS AND DISCUSSION

EDX spectra of the starting material at ambient conditions show a clean hcp structure with no detectable oxide peaks (Fig. 1). Measured lattice parameters of $a = 3.5885$ and $c = 5.6434 \text{ \AA}$ are consistent with the literature values.⁴ On compression, we observe the standard rare earth crystal sequence in good agreement with the literature. Fig. 1 shows the EDX spectra for the different phases obtained on compression. Following the initial hcp spectra, we observe the Sm₃ structure at 6.0 GPa and the dhcp at 15.1 GPa. Although we never observe a pure fcc phase, the fcc stability region may lie between our pressure steps (37 to 43 GPa). The fcc stability field is known to narrow considerably in heavy rare earth metals and our high pressure results suggest that the fcc stability field in Dy is less than 6 GPa. Upon increasing pressure to 43.0 GPa, we find the completion of the hcp → fcc transition.

The structure of the fcc phase has been the subject of some debate. A careful refinement of the fcc phase in Pr found a hexagonal cell with $Z = 24$ (denoted hR24) to be the best fit. ¹⁰ hR24 belongs to group R-3m with atoms occupying the 6c and 18h sites. Table I gives the indexing for hR24 at 61.6 GPa, with lattice parameters $a = 5.7032$ and $c = 13.9721$. The atomic positions given by Hamaya et al.¹⁰ were used for structure assignment, and not refined further. The measured and calculated d -spacings are in good agreement, however, evidence of preferred orientation is seen in the differences in the measured and calculated intensities. Pure hR24 exists until at least 69.4 GPa, followed by a phase transition at 73.3 ± 3.9 GPa. We find a simple body centered monoclinic (bcm) structure best explains the spectra acquired above 74 GPa.

Bcm phases are also observed in Ce(α'' -Ce)¹¹ and Gd¹² under pressure. Our data more closely resemble Gd as indicated by the indexing shown in Fig. 2. The slight variation in the bcm cells of Ce and Dy may result from the intermediate hR24 phase found in Dy but not in Ce.

Gd also has an intermediate distorted fcc phase although it was indexed as a 6-layered hexagonal.¹² A mixture of hR24 and bcm is observed until 81.8 GPa. Fig. 2 shows the bcm phase at 81.8 GPa as well as at 118.6 GPa, the highest pressure attained in this study. The bcm phase has lattice parameters $a = 2.6932$, $b = 2.1728$, and $c = 4.3534 \text{ \AA}$, with $\beta = 92.61^\circ$ at 118.6 GPa. The d-spacings are given in Table II. Calculated bcm structures show a large (110) peak. We observe a weak (110) peak at 81.8 GPa, most likely due to sample texturing, and this peak is totally obscured at 118.6 GPa by the diamond absorption edge.

The pressure -volume EOS for Dy is shown in Fig. 3. The solid curve is a 3rd order Birch - Murnaghan fit, given by

$$P = \frac{3}{2} K_0 \left(x^{\frac{2}{3}} - x^{\frac{5}{3}} \right) \left[1 + \frac{3}{4} \left(K'_0 - 4 \right) \left(x^{\frac{2}{3}} - 1 \right) \right], \quad x = \left(\frac{V_0}{V} \right). \quad (2)$$

V_0 is the volume at ambient conditions, K_0 is the isothermal compressibility, and K'_0 is the first derivative of K_0 . The compression of Dy is continuous for all structures through hR24. The hR24 \rightarrow bcm transition, however, is accompanied by a 6% volume change, following which Dy becomes much less compressible. Previous studies⁵ found $K_0 = 37.8(9)$ GPa and $K'_0 = 2.8(1)$ GPa. We find $K_0 = 36.22$ GPa and $K'_0 = 3.29$ GPa for the pre-collapse phases, and $K_0 = 24.08$ GPa and $K'_0 = 4.06$ GPa for the bcm phase.

Of the rare earth elements in which low-symmetry phases have been observed to follow the fcc phase, Ce, Pr, and Gd show discontinuous transitions, while Nd and Sm do not. These phase transitions have been associated with f-electron participation in bonding, and it is known from the actinide elements that bonding f-electrons favor low-symmetry structures. For the lanthanides, as pressure increases, f-electrons begin to participate in bonding, therefore at some

point in the compression of the rare earth metals, it will be energetically favorable to transform to a low-symmetry structure. The bcm phase of Dy (similar to that found in Gd) has $c > b$, while the bcm phase for Ce has $b > c$. Ce undergoes an isostructural phase transition (fcc \rightarrow fcc'), which is associated with f-electron delocalization, before transforming to bcm. Dy and Gd transform from m-fcc phases to bcm, with this transition being the f-electron delocalization. The non-isostructural nature of this transition has been attributed to the interactions of multiple f electrons.¹² Thus the differences in the bcm cells for Dy and Ce may be a result of the transformation path from the preceding phases, as well as contribution from bonding f electrons.

CONCLUSIONS

In summary, the fcc phase of Dy has been indexed to an $\text{hR}24$ structure in the pressure range between 43 GPa and 73 GPa. In addition, Dy is shown to have a volume change of 6% at 73.3 GPa, corresponding to an $\text{hR}24 \rightarrow \text{bcm}$ transition. We attribute this transition to the delocalization of the 4f electrons. The body-centered monoclinic phase (similar to that observed in Gd) is seen to be stable at ~ 118.6 GPa, at which the volume compression is $V/V_0 = 0.402$. Theoretical first-principle calculations on dysprosium metal are needed for the proposed crystal structures in order to confirm their stability and establish the electronic structure at high compressions.

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FIGURE1

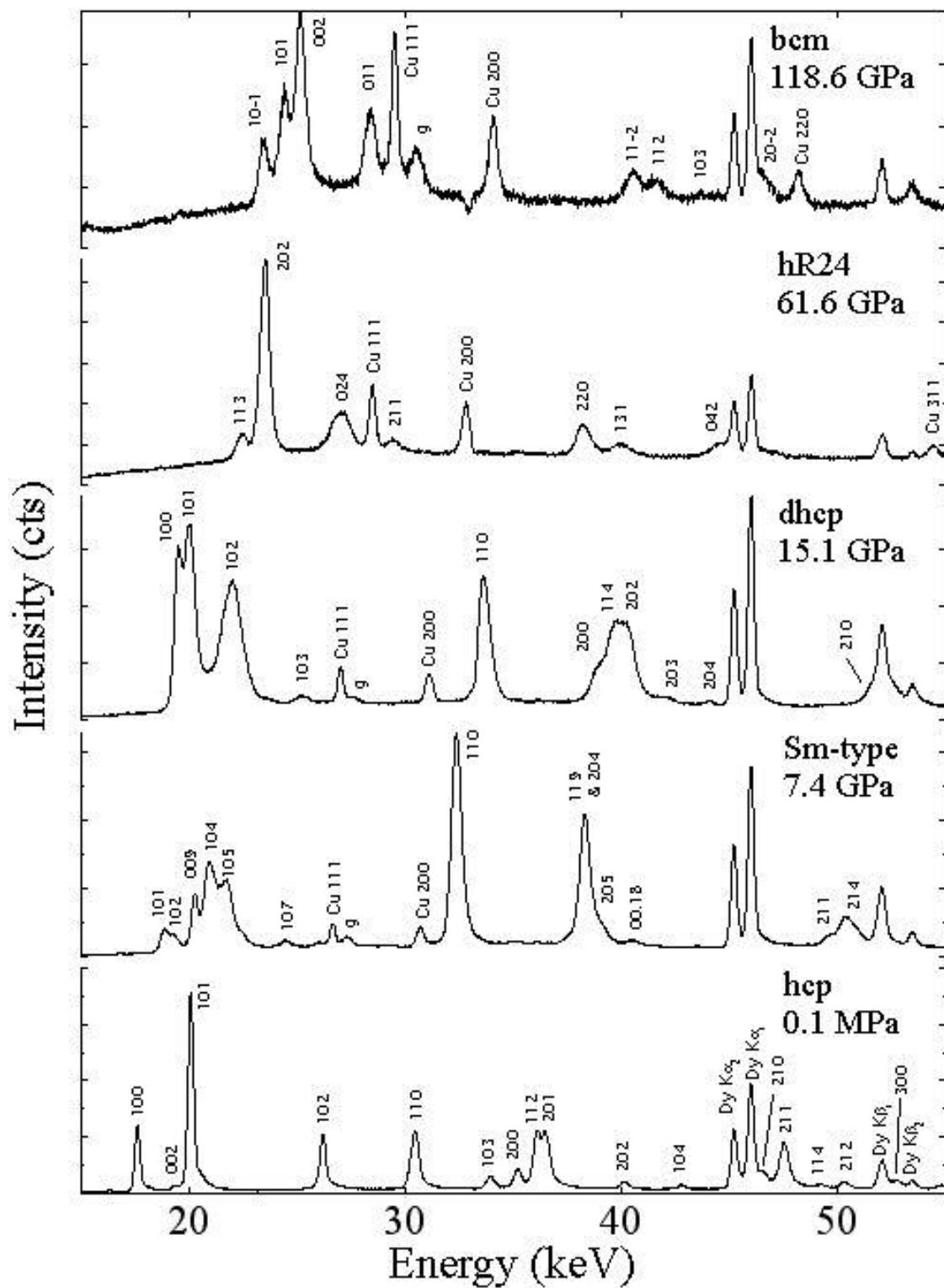


FIGURE 2

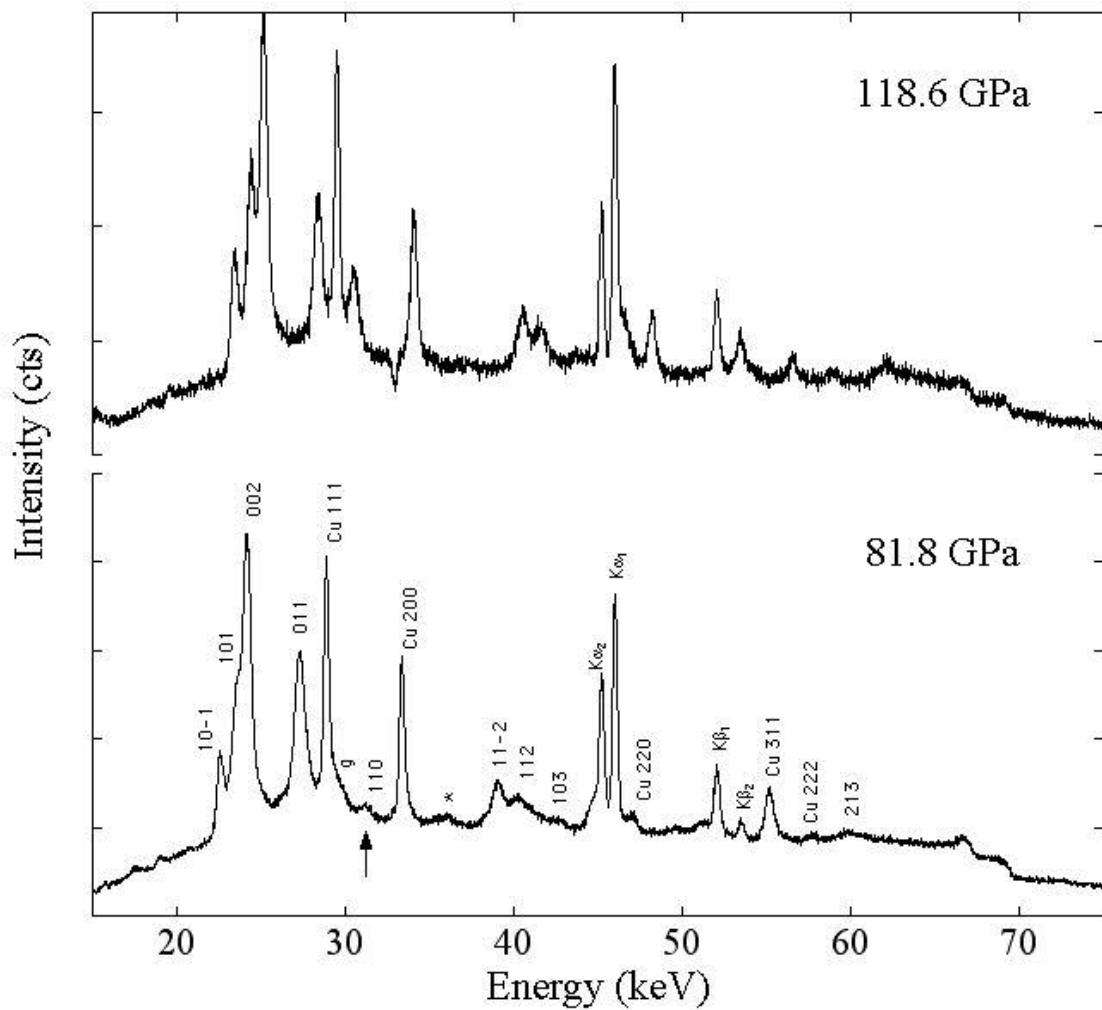
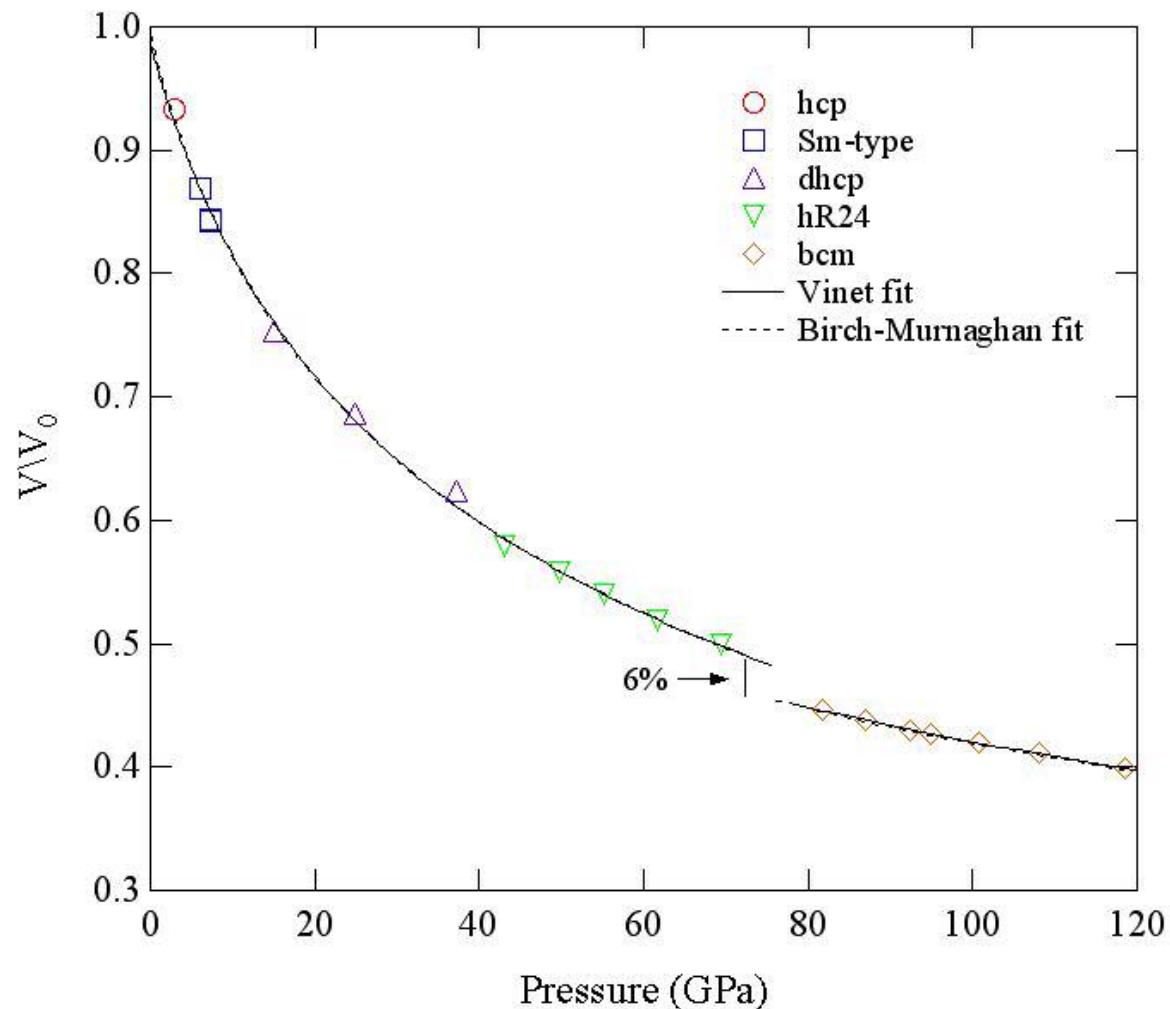


FIGURE3



TABLEI.Observedandcalculateddd - spacingsandintensitiesforthehR24phaseofDyat61.6

GPa.Thesampleshowsevidenceofpreferredorientationasseeninthe discrepancybetweenthe observedandcalculatedintensities.

hkl	d_{obs}	d_{calc}	I_{obs}	I_{calc}
113	2.4452	2.4320	0.52	2.2
202	2.3271	2.3283	4.0	100
024	2.0230	2.0166	100	85.0
211	1.8569	1.8504	19.4	2.3
033	1.5588	1.5522	18.3	4.4
220	1.4301	1.4258	70.0	39.3
042	1.2295	1.2159	24.1	17.1
422	0.9306	0.9252	11.2	7.7
244	0.8861	0.9018	11.5	6.5

TABLEII.Observedandcalculateddd - spacingsandintensitiesforbody - centeredmonoclinicDy

at118.6GPa.Sampletexturingisstillprominentasseenintheintensitiesaswellastheabsence ofthe110peak.

hkl	d_{obs}	d_{calc}	I_{obs}	I_{calc}
10-1	2.3351	2.3361	4.7	32.9
101	2.2425	2.2428	7.1	37.8
002	2.1744	2.1745	14.3	41.3
011	1.9272	1.9276	100	100
11-2	1.3495	1.3480	36.0	64.3
112	1.3137	1.3114	23.1	59.2
20-2	1.1695	1.1680	36.5	19.5
213	0.8807	0.8800	10.1	62.1

FIGURECAPTIONS

FIG.1.EDXD spectra of Dy on compression. All observed phases of Dy to 119 GPa are shown in this figure along with the (hkl) assignments of various diffraction peaks in each spectrum.

FIG.2. Diffraction spectra of body-centered monoclinic Dy in the ultrahigh-pressure range between 81 GPa and 119 GPa. The diamond absorption edge becomes apparent in the spectrum at 119 GPa obscuring the weak (110) diffraction peak from the sample.

FIG.3. The measured equation of state for various phases of Dy to 119 GPa at room temperature. The solid curves are the fits to the Birch-Murnaghan and Vinet equations described in the text. The volume change of 6% at the 73 GPa phase transition is clearly evident.