Reports

X-ray Diffraction Studies on Dysprosium at High Pressures

Abstract. *Dysprosium has been studied at pressures up to about 160 kilobars, well above the transition reported near 50 kilobars by other workers. It shows no definite structural alteration from hexagonal close-packed structure throughout this range. It is suggested that the 50-kilobar transition is most likely electronic or magnetic in nature, or that the metal undergoes a hexagonal stacking rearrangement.*

In a study of rare-earth metals, Bridgman (*1*) reported a cusp in the electrical resistance of dysprosium occurring around 70 kb. This figure should be altered to about 55 kb after the revision of the electrical resistance pressure scale by Kennedy and LaMori (*2*). Bridgman's (*1*) volume measurements extended only to pressures of 40,000 kg/cm^2, too low for transitional effects. More recently Stager and Drickamer (*3*) have observed the same effect in the electrical resistance of dysprosium under pressure. Souers and Jura (*4*) have studied extensively the phase diagram of dysprosium and have measured the pressure effect over a range of temperature.

I decided to conduct an x-ray investigation on dysprosium at pressures above its reported transition to find out what alteration occurs in its normally hexagonal close-packed structure.

The basic techniques used for these high pressure x-ray studies have been described (*5*). The dysprosium was supplied to me by George Jura and is from the same supply that was used in Souers and Jura's study (*4*). For each run, freshly filed material was mixed with approximately six parts of amorphous boron. An internal pressure standard (NaCl or LiF) was used in the proportion 1 : 1 in many runs.

Exploratory runs were made with taper-face pistons, without any internal standard, to avoid complications from the standard's additional lines in the diffraction patterns. The characteristics of the apparatus are sufficiently well-known so that an estimate of the pressure in these runs—150 kb—is reliable. The runs revealed no alteration in the structure of dysprosium from hexagonal close-packed (hcp). This statement is made on the evidence of several sets of data comparable to that of Table 1. The small number of lines (missing lines may all be accounted for by orientation effects or structural deterioration) might make this identification hazardous, but it seems improbable that a radically new phase would have very many lines coincident with those of hcp unless a stacking rearrangement such as that found in Sm and Gd by Jayaraman and Sherwood (*7*) had occurred. To investigate this further, it was necessary to study the behavior of dysprosium as a function of known pressures.

Sample pressures in the boron-cell techniques are best measured by using an internal standard whose volume change with pressure is already known (*5*). In previous work (*8*), I used Bridgman's (*9*) volume data, for pressure of 100,000 kg/cm^2, on NaCl for this purpose. In the present work it was necessary to use pressures much higher than Bridgman's. Hence the "20°C curve" from Christian's (*10*) shock-wave study of alkali halides was adopted. With its large compressibility and cubic structure, NaCl in general makes a good internal pressure gage. However, in this dysprosium study a difficulty did arise, namely the 111 and 200 reflections of NaCl interfered with the 10•0, 00•2, and 10•1 reflections of dysprosium. Mixtures of NaCl and Dy (with boron) in general at high pressures gave patterns in which only the Dy 11•0 and the unresolved 11•2 and 20•1 could be measured. Hence, in those patterns only the value for the parameter *a* of Dy could be obtained. The use of LiF as an internal pressure gage proved more satisfactory from the standpoint of x-ray diffraction, especially at pressures above 100 kb. The compression of LiF was obtained by a smooth extrapolation of Bridgman's data for 40,000 kg/cm^2 (*11*) to join that of Christian (*10*). The obvious hazard of such a long interpolation was vitiated by finding that pressures obtained from LiF and NaCl were consistent in pressure runs of mixtures of the two. Also, in graphs of the *a* parameter as a function of pressure determined by either standard, no systematic deviations appeared. Runs of this type, with tapered pistons, were adequate to determine the pressures of diffraction patterns which had shown only hcp dysprosium to be as high as about 160 kb. However, to study the immediate neighborhood of the reported transition a more refined approach was necessary.

It was discovered that when flat-faced pistons are used the boron annulus could be replaced by an annulus of polystyrene surrounding the sample. A disc initially about 0.06 cm in height and 0.3 cm in diameter is punched from a sheet of plastic. A 0.04-cm hole is drilled in its center for the sample. On initial application of load, the plastic extrudes laterally to a quasi-equilibrium thickness of 0.01 to 0.02 cm at which time the sample is under quite high pressures. If the plastic annulus is too thick or the loading too abrupt, the lateral extrusion of the plastic is explosive in nature and only a film remains. Pressures have been retained in a properly loaded annulus for periods of 4 weeks. The polystyrene gives rise to a uniform background in the diffraction patterns rather than to the banding characteristic of amorphous boron. It is quite possible that a better performing plastic than polystyrene can be found but to date no search has been made. The main advantage of the combination of plastic annulus and flat piston face is that better control of pressure can be obtained in the range below 100 kb. Several runs have been made of the dysprosium-NaCl (boron) mixture to determine the variation of the hexagonal lattice parameter *a* with pressure. The data obtained from the most prolonged and extensive run on one sample (some 19 exposures taken over about

Table 1. Measurements on dysprosium. The parameters of sample 248-5 are $a = 3.223$ Å, $c = 5.044$ Å; those of sample 265-2 are $a = 3.402$ Å, $c = 5.280$ A.

hk·l	Sample 248-5, 160 kb (approx)		Sample 265-2, 65 kb (approx)	
	d_{calcd} (Å)	d_{obs} (Å)	d_{calcd} (Å)	d_{obs} (Å)
10·0	2.791	2.800	2.946	2.935
00·2	2.522		2.640	2.640
10·1	2.442	2.442	2.573	2.564
10·2	1.871		1.966	
11·0	1.611	1:607	1.708	1.707
10·3	1.440		1.511	
20·0	1.396	1.357	1.473	1.449
11·2	1.358		1.430	
20·1	1.345		1.419	
21·0	1.055	1.033	1.113	1.100
21·1	1.033		1.089	
30·0	0.930	0.928	0.982	

4 weeks' time) are presented in Fig. 1. The experimental error displayed is ±0.0035 in the ratio from the limits of precision of the measurement of 2θ on the films. The accuracy of the determination of pressure is dependent on the accuracy of Christian-Bridgman (*10*) data for NaCl volume. I believe this is accurate to at least 5 kb at 100 kb but an independent check would be desirable. The precision of the pressure measurement is greater. The *a* spacing of NaCl is determined to a precision corresponding to less than ±2 kb on the NaCl scale. As can be seen in Fig. 1, the data may be fit equally well by a smooth curve without break, two curves with a break (say at 50 kb) of about 0.005 in a_p/a_o, or by a smooth curve with two slight reversals in curvature above 50 kb. All of these interpretations lie within the experimental error.

From runs with no pressure standard, *c* or the ratio *c*/*a* was determined as a function of *a* whose pressure dependence had already been determined. Graphs of λ ($\lambda = c/a$) plotted against *a* revealed that no fit higher than first order was necessary or justified. Again small breaks in the plot or changes in curvature could be missed; however there was no firm evidence for such behavior. The data was fit to $\lambda_p/\lambda_o = 1 \pm 0.1308\ (1 - \epsilon)$ by the method of averages. In this expression $\epsilon = a_o/a_p$ and a_o is taken to have the value 3.5903 Å given by Spedding *et al.* (*12*). By using λ_p/λ_o and a_p/a_o from all internal standard runs the compilation of V_p/V_o given in Fig. 2 may be obtained. Again, the lack of any significant discontinuity either in V_p/V_o or its derivatives is obvious. There does seem to be a gap between the Bridgman data and mine, as also appears in Fig. 1, but this is still within the experimental error of both sets of data. It is very difficult to collect data with the x-ray technique in the Bridgman range since even the gentlest loading usually produces higher pressures. This explains the scarcity of x-ray data at pressures less than 40 kb.

In order to explain the discrepancy between the apparently negative x-ray results and the electrical resistance measurements on dysprosium in which the resistance measurements seem definitely to indicate a polymorphic transition at about 50 kb, while the x-ray results show no evidence of structural change at pressures some 3 times higher, I would like to offer several hypotheses.

1) A true structural alteration occurs normally at about 50 kb in dysprosium which did not occur for some unknown reason in all the x-ray studies. Since this is the same sample material used by Souers and Jura (*4*) in their study and, in addition, the x-ray cell is a high-shear environment which should aid transitions, I deem this improbable.

2) A true structural alteration occurs but the x-ray data have been collected only on the residual untransformed hcp because (i) the lines of the new phase are almost coincident with those from the residual hcp or (ii) the new phase forms in domains too small to give a coherent x-ray diffraction pattern. Neither of the two halves of this hypothesis can be completely discarded, although the second seems physically somewhat more plausible.

3) The transition in dysprosium is electronic in nature, either of first or higher order, involving an alteration in the number of 4*f* electrons but no change in structure type as is already known for face-centered cubic (fcc) cerium (*13*). This hypothesis deserves more extensive discussion. Under normal conditions of pressure and temperature solid dysprosium may be regarded as possessing nine 4*f* electrons in localized orbits and a conduction band formed from three electrons per atom which, in the free state, would be the $6s^2$ and $5d^1$ electrons. The promotion of one 4*f* electron would reduce the localized number to eight. In cerium the analogous (ideal case, neglecting fractional valency effects due to temperature and pressure) picture is the change from a state containing one localized 4*f* electron to one containing none. As temperature increases, the transition pressure increases, and along this curve the volume difference decreases to zero and the transition becomes of higher order (*14*). If dysprosium is to be considered an analogous case, its permitted volume change (from the experimental data) is quite small, and the critical temperature for the transition lies near or below room temperature. In the case of cerium, the major portion of the entropy difference between the two fcc phases can be ascribed to the degeneracy of the one 4*f* electron of the expanded phase. The magnitude of such entropy contributions may be approximated (*15*) by *R*ln (2J+1). For cerium this amounts to about 3.56 cal per mole per degree Celsius. If dysprosium changes from the nine 4*f* electron configuration to eight the magnetic entropy contribu-

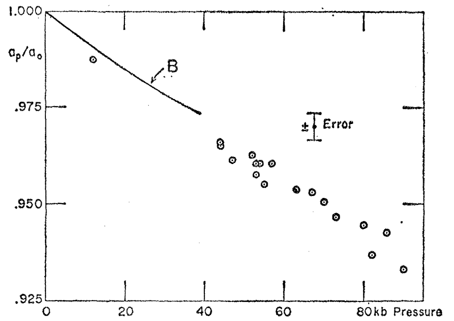

Fig. 1. Compression of *a* axis in dysprosium under pressure (one run only); *B* denotes the same quantity derived from the data of Bridgman.

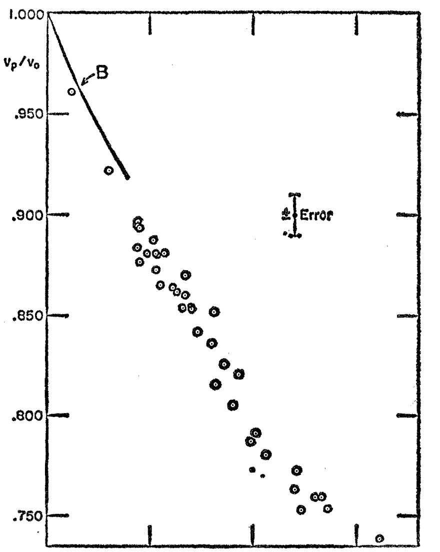

Fig. 2. The volume compression of dysprosium; *B* denotes the data of Bridgman.

tion is 5.50–5.08 which equals 0.42 cal per mole per degree Celsius. This would be only a small contribution to the change in entropy, ΔS, in $dP/dT = \Delta S/\Delta V$, and hence for a ΔV comparable to that of the cerium case dP/dT would be small as found by Souers and Jura (*4*). However, my x-ray data seem to rule out any such large ΔV. A small ΔV puts no constraint on dP/dT. Dysprosium is known (*16*) to adopt the ionic quadrivalent state but with much more difficulty than cerium. Recent estimates (*17*), of the metallic radius of a hypothetical quadrivalent dysprosium are about 1.61 Å at 1 bar. The Bridgman (*18*) data on quadrivalent cerium (above 30 kb) may be used to estimate the effect of pressure on this parameter. It should be about 1.55 Å at 50 kb and 1.51 Å at 100 kb. Since this is a nonideal hcp structure the average between the two "nearest neighbor" distances is used. Corresponding values from the x-ray data are 1.77Å for 1 bar, 1.70 Å for 50 kb, and 1.64 Å for 100 kb. There is no coincidence within this range. Nor does the assumption that the transition occurs at a valency of 3.5 mend the situation since Dy with a valence of 3.5 should have a radius of 1.69 Å at 1 bar and would presumably decrease to about 1.62 Å at 50 kb and 1.59 Å at 100 kb, again not consistent with the x-ray data. I conclude that unless the current (*17*) metallic radii estimates are grossly in error, this transition is not electronic 4*f*-type as in cerium. However, it might still be isostructural electronic in nature. Both cerium and lanthanum (*19*) have been reported as existing in fcc forms with two different lattice spacings. These differences are less than 1 percent. This phenomenon might be occuring in dysprosium.

4) The transition in dysprosium is a stacking arrangement of hexagonal close packing from the normal arrangement of layers parallel to *c* to an alternative form, such as the La structure or the Sm structure. The La structure double hcp is derived from normal hcp by doubling the *c* axis parameters. All lines *hk·l* from normal hcp appear as *hk·2l* in the double hcp form plus additional lines *hk·l′* in which *l′* is odd. These added lines may be weak and missed in the high pressure studies. Hence the available data does not contradict this double hcp structure for dysprosium. The position of the expected lines were calculated, and the films inspected closely in those regions. None could be found. This can not be regarded as conclusive since lines of known structures (*5*) are frequently absent in high pressure films owing to orientation effects and to line broadening (to the point of loss in the background) because of structural faulting. Since this structure was quenched in from high pressures in samarium by Jayaraman and Sherwood (*7*), its occurrence in dysprosium would not be unusual but definite proof is lacking. The data can also be tested for the (normal) Sm structure. Since this is rhombohedral, most of its diffraction lines do not coincide with hcp. The available data, even allowing for multitudinous absences, do not permit such indexing, hence the most probable stacking alteration, if the transition is to be such, is to the La arrangement. Other hypothetical stacking arrangements, such as other even multiples of the hcp parameter *c* are possible but not demanded by the data. Samples on release of pressure showed neither the La or Sm structures, however a weak array of extra reflections did appear in the "after" patterns. These could all be accounted for by a cubic indexing (fcc extinctions) $a = 5.212 \pm .003$ Å or equally well as $a = 10.425 \pm .006$ Å, which is almost certainly Dy_2O_3 although the lattice parameter differs appreciably from $a = 10.665$ Å of Swanson *et al.* or the $a = 10.613$ Å of Zachariasen (*20*). Normal hcp lines in the same patterns showed no such displacement. This oxide must have formed in or on the highly strained samples after release of pressure. The deviate *a* value may be due to its coherence to a Dy matrix or to nonstoichiometry.

5) For the sake of completeness, it is necessary to mention that the transition in dysprosium might be one to an alternate symmetry such as orthorhombic in which the parameter change is minor and leads only to line splitting and the addition of faint extra lines. The high-pressure data is completely inadequate to prove this possibility.

6) The transition in dysprosium may be magnetic ordering as suggested by Souers and Jura (*4*), either without change in crystal symmetry or a small deviation as in hypothesis 5.

In conclusion I believe either the small ΔV, noncerium type transition in hypothesis 3, the stacking rearrangement of hypothesis 4, or the magnetic transition of hypothesis 6 is the most likely. In the event that it can be proved that the third is correct, electronic transitions of this type are very likely a phenomenon characteristic of all of the rare-earth metals, since dysprosium with its nine 4*f* electrons would not seem to have any special disposition to this behavior. Equally so, if hypothesis 4 proves correct, this work, together with that of Jayaraman and Sherwood (*7*), suggests a common phenomena in all hcp or double hcp rare earths in the absence of other transitions.

JOHN C. JAMIESON

Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637

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23 April 1964