Solid-Liquid and Solid-Solid Transformations in the Rare-Earth Metals at High Pressures

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The fusion behavior and solid-solid transformations in the rare-earth metals have been investigated at pressures in the range 6–65 kbar. The phase diagrams are presented for La, Pr, Nd, Sm, Gd, and Tb. The initial melting slopes of Dy to Lu have been obtained. Since most of the rare-earth (R.E.) metals melt from a bcc structure, they offer a series for comparison. When the initial melting slope is plotted against atomic number they fall into groups according to their valency; the typically divalent metals Eu and Yb in one, and the typically trivalent metals La, Gd, and Lu in another. Samarium and the metals from Tb to Tm have melting slopes which are intermediate between those of the typically divalent and trivalent metals. It is suggested that these metals assume a partial divalent character in the liquid state and possibly also in the bcc phase. This suggestion derives support from the fact that the gaseous neutral atoms of the R.E. elements, with the exception of La, Gd, and Lu, have no $5d$ electron and are therefore divalent. Cerium exhibits a unique fusion behavior and its negative melting slope has been attributed to the tetravalency ($4f \rightarrow 5d$ electron promotion) of the atoms in the liquid. For the very small melting slope of Pr, it is suggested that the atoms in the liquid have partial tetravalent character due to $4f \rightarrow 5d$ electron promotion. Comparisons with alkali metals are made and it is deduced that the R.E. metals are quite compressible at high temperatures. Pressure induced transformations in the rare-earth metals are in the sequence hcp $\rightarrow$ Sm-type $\rightarrow$ double hcp $\rightarrow$ fcc. A plausible mechanism based on the variation of c/a ratio with pressure is discussed for hcp $\rightarrow$ Sm-type transformation.

INTRODUCTION

THE phase diagrams of Eu, Yb,[1] and Ce[2] were recently reported. Europium has been found to exhibit a fusion-curve maximum at about 35 kbar and 995°C, and Ce a fusion-curve minimum at about 33 kbar and 662°C. The broad minimum in Ce was interpreted as a reflection of supercritical behavior in the neighboring fcc-Ce. In the context of these interesting fusion properties it appeared worthwhile to pursue high-pressure, high-temperature studies on other rare-earth metals. In this paper the results of such studies are reported.

EXPERIMENTAL

A piston-cylinder device was used to generate pressures. Pressures to 45 kbar were attained using an unsupported tungsten carbide piston, and higher pressures by the double staging technique[3] in which the piston received support. Samples were encapsulated in Ta or Nb containers. The purity of the samples was given as 99.5%. Melting points and the fcc-bcc transformation temperatures were determined by the method of differential thermal analysis (D.T.A.).[4] The thermal arrests associated with melting as well as the solid-solid transitions were very strong and sharp in all cases.

Temperatures were measured using Chromel-Alumel or Pt-(Pt 10% Rh) thermocouples. The Chromel-Alumel couple undergoes a progressive deterioration on prolonged use at temperatures above 900°C. Thus, when a second set of measurements was made during a run, the transformation temperatures fell about 25° below those of the first set. In order to collect reliable data, it was necessary to cover the pressure range in three or more separate runs, obtaining one or two transformation temperatures each time. At temperatures about 1000°C, Chromel-Alumel appears to deteriorate so rapidly that its use must be avoided. This problem of thermocouple deterioration was greatly minimized by the use of a Pt-PtRh thermocouple. To give some idea of the relative performance near 1100°C, the fusion data of Sm may be quoted. The data obtained using Chromel-Alumel couples fell about 50° below those of the determinations made with Pt-PtRh couples. With the latter, a progressive deterioration was noticed when the conventional BN sleeve was used to surround the junctions. This difficulty was eliminated by surrounding the end of the assembly with crushable alumina ceramic.

In experiments below 1000°C, where both the thermocouples could be relied upon, the transformation temperatures measured with the Pt-PtRh couple were lower than those obtained using Chromel-Alumel. This behavior is in accordance with the findings of Bundy[5] and Hanneman and Strong[6] who report a larger negative pressure effect for the thermal emf of a Pt-PtRh couple than for a Chromel-Alumel thermocouple. At high pressures ($\sim$40 kbar) and high temperatures ($\sim$1200°C) the effect assumes serious proportions (positive corrections of about 40°) and it becomes necessary to apply corrections to the data to avoid misinterpretation. Hanneman and Strong[6] have not only compared the

[1] A. Jayaraman, Phys. Rev. **135**, A1056 (1964).

[2] A. Jayaraman, Phys. Rev. **137**, A179 (1965).

[3] A. Jayaraman, W. Klement, Jr., R. C. Newton, and G. C. Kennedy, J. Phys. Chem. Solids **24**, 7–18 (1963).

[4] G. C. Kennedy and R. C. Newton, *Solids under Pressure* (McGraw-Hill Book Company, Inc., New York, 1963), pp. 163–174.

[5] F. P. Bundy, J. Appl. Phys. **32**, 483 (1960).

[6] R. E. Hanneman and H. M. Strong, J. Appl. Phys. **36**, 523 (1965).

TABLE I. Transformation temperature °C (uncorrected) measured with Pt-(Pt 10% Rh) couple.[a]

Pressure kbar	La S-S	La S-L	Pr S-S	Pr S-L	Nd S-S	Nd S-L	Sm S-S	Sm S-L	Gd S-S	Gd S-L	Tb S-S	Tb S-L
6	887	925	802		855	1035						
8				805			931	1120	1235	1350	1310	1420
10	905	935	815		858	1039	925					
14	923	941	825		864	1046	920	1130	1230	1365	1320	1455
17.5	942	945	834		870	1050	916		1226	1390	1310	1470
21		952	840				918	1140				
25		964	853	915	881	1055	921	1146	1225	1400		
29		972	858	910	898	1055	924	1150	1220	1410		
33		980			904	1055			1214	1420		
37		986	875	900	913	1053	928	1155	1210	1430		
41		996			922	1053	932	1160				
63							931	1145				

[a] S-S is solid-solid transformation; S-L is melting.

relative effects for Chromel-Alumel and Pt-PtRh thermocouples but have also proposed absolute correction factors for the two thermocouples. The data obtained using the Pt-PtRh couple have been corrected using these factors, and plotted in the phase diagrams. In the case of Pr, measurements were made with Chromel-Alumel thermocouple. The uncorrected data for all the metals studied have been presented in Tables I and II. The temperatures are believed correct to ±5°. The pressures are believed to be true to ±1 kbar below 40 kbar and to ±2 kbar at pressures higher than this.

RESULTS

Lanthanum

Figure 1 is the phase diagram of La. The melting point as well as the fcc-bcc transformation temperature increases with pressure, the latter much more rapidly. A triple point between fcc, bcc, and liquid is located at about 19 kbar and 967°C.

The cusp in resistivity noted by Bridgman[7] at about 25 kbar at room temperature has been shown to be due to a sluggish transformation in La from the double hexagonal close-packed (dhcp) to the fcc structure.[8] The phase boundary worked out by McWhan et al.[9] has a

TABLE II. Transformation temperature °C (uncorrected) measured with Pt-(Pt 10% Rh) couple.[a]

Pressure kbar	Dy S-S	Dy S-L	Ho S-S	Ho S-L	Er S-S	Er S-L	Tm S-S	Tm S-L	Lu S-S	Lu S-L
6	1425	1495	1535	1570	None	1610	None	1636	None	1710
14				1620						
25	1430	1545								

[a] S-S is solid-solid transformation; S-L is melting.

[7] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81,** 165 (1952).
[8] D. B. McWhan and W. L. Bond, Rev. Sci. Instr. **35,** 626 (1964).
[9] D. B. McWhan, P. W. Montgomery, H. D. Stromberg, and G. Jura, J. Phys. Chem. **67,** 2308 (1963).

negative slope and its intersection with the temperature axis is in agreement with the known dhcp-fcc transformation temperature at atmospheric pressure.

Praseodymium

Figure 2 is the phase diagram of Pr. The transformation temperatures were obtained using both Chromel-Alumel and Pt-PtRh couples. When the data obtained from the latter couple are corrected for the relative pressure effect on the thermal emf, the agreement with Chromel-Alumel is very good. In the figure, the data obtained with Chromel-Alumel are plotted. The different symbols stand for different runs. Piermarini and Weir[10] have reported a transformation of dhcp-Pr to the fcc structure at pressures above 40 kbar at room temperature. Bridgman[7] found a cusp in the resistance of
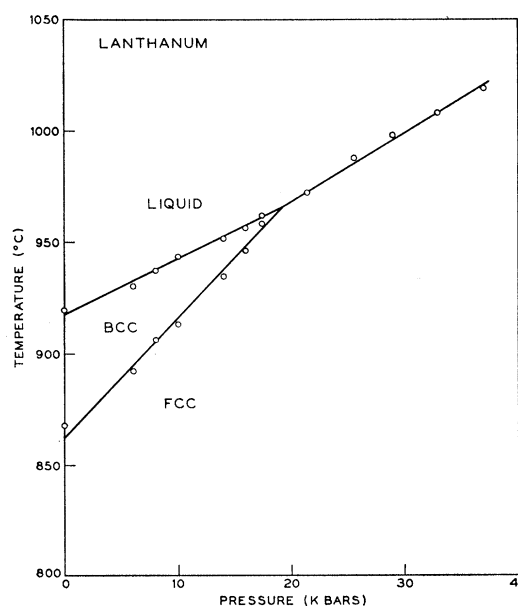

FIG. 1. Phase diagram of lanthanum.

[10] G. J. Piermarini and C. E. Weir, Science **144,** 69 (1964).
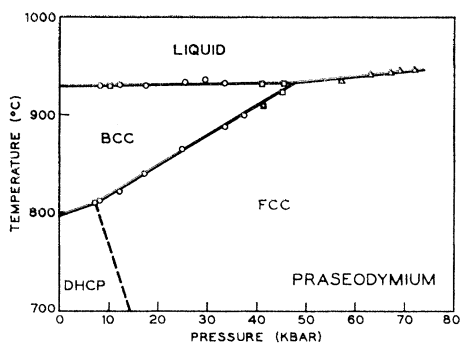
FIG. 2. Phase diagram of praseodymium.

Pr at about 39 kbar (revised pressure) which probably is due to the transformation from dhcp to fcc. No attempt was made to follow this phase boundary in the present study. However, a distinct break in the slope was evident when following the bcc transformation, and this is interpreted as the meeting point of the dhcp-fcc phase line. Accordingly, a boundary is indicated by the dashed line. The triple-point coordinates for fcc-bcc-liquid and dhcp-fcc-bcc are (48 kbar 938°C) and ($\sim$8 kbar, $\sim$810°C), respectively.

Neodymium

Figure 3 is the phase diagram of Nd. A transformation to fcc was reported by Piermarini and Weir[10] at about 50 kbar. The bcc boundary very clearly shows a break which presumably is due to the intersections of the dhcp-fcc boundary. To the highest pressures reached in the present study, the fusion curve and the fcc-bcc boundary do not meet.

Samarium

Figure 4 is the phase diagram of Sm. The points appearing below the phase boundaries represent uncorrected data obtained with a Pt-PtRh thermocouple. A curve drawn through the latter fusion data would have a maximum, and this would lead to misinterpretation. The example of Sm thus shows the importance of correcting the data for the pressure effect on thermal emf, when using Pt-PtRh thermocouples. The bcc phase line has a break in the slope at about 18 kbar which is believed to be due to the intersections of the rhombohedral-dhcp boundary. The latter transformation was reported recently[11] and it was found that the dhcp form could be retained metastably at atmospheric pressure.

Gadolinium

Figure 5 is the phase diagram of Gd. The fusion curve does not have any unusual feature. The hcp-bcc

phase boundary has a break in the slope at 8 kbar and this is believed to be the intersection of the hcp-rhombohedral (Sm-type) boundary. The latter transformation was reported by Jayaraman and Sherwood,[12] who found that the high-pressure Sm-type phase could be metastably retained at atmospheric pressure and room temperature. The transformation to Sm-type phase was found to be complete when samples were pressurized at temperatures near 300°C. Bridgman[13] in his studies on Gd found a resistivity anomaly near 25 kbar. This is undoubtedly related to the latter transformation. The hcp-rhombohedral line was not pursued.

The hcp-bcc as well as the Sm-type-bcc boundaries in Gd have negative dT/dP, indicating that the bcc phase is denser than the hcp or Sm type. A decrease in resistance may be expected in general for a transformation from hcp to bcc if the latter phase turns out to be denser. The observation of Spedding et al.[14] of a resistance decrease at 1261±14°C for Gd at atmospheric pressure is therefore in line with this.

Terbium, Dysprosium, and Holmium

Figure 6 is the phase diagram of Tb. Excursions to higher pressures were limited by the high temperatures involved and attendant problems. With Dy the solid-
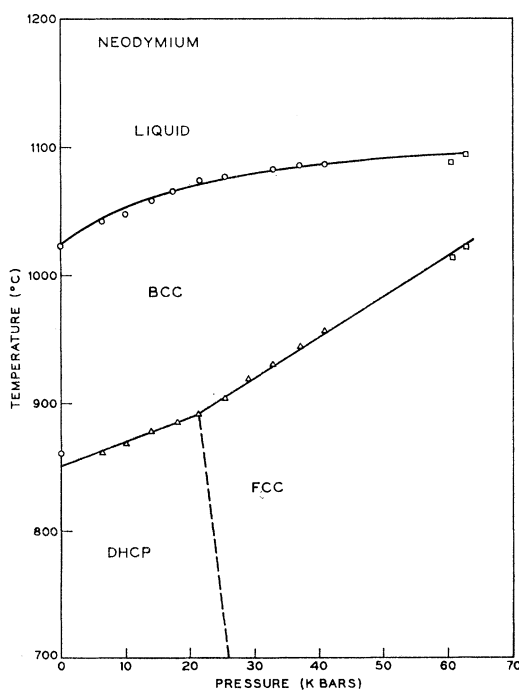

FIG. 3. Phase diagram of neodymium.

[12] A. Jayaraman and R. C. Sherwood, Phys. Rev. Letters 12, 22 (1964).

[13] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 82, 95 (1953).

[14] F. H. Spedding, J. J. Hanak, and A. H. Daane, J. Less-Common Metals 3, 110 (1961).

[11] A. Jayaraman and R. C. Sherwood, Phys. Rev. 134, A691 (1964).

solid transformation and fusion were determined at 8 and 25 kbar; with Ho these were carried out at 8 kbar.

Bridgman[15] reported a cusp in resistivity in Dy at about 50 kbar and in Ho at about 30 kbar. Stromberg and Stephens[16] find in Tb a resistance anomaly at about 27 kbar. McWhan and Stevens[17] have recently concluded from their high-pressure x-ray and magnetic studies, by analogy with the behavior noted in Gd, that the anomalous resistance behavior encountered in these is in all probability due to a phase change to the Sm-type structure.

Spedding et al.[14] report an abrupt decrease in resistance in the case of Tb and an increase in resistance for Dy and Ho at 1316±10°C, 1392±8°C, and 1442±8°C, respectively, at atmospheric pressure. These changes are believed to be due to a transformation to the bcc structure. While the initial slopes of the phase boundaries of Dy and Ho are definitely positive, in the case of Tb there is some uncertainty. However, the decrease in resistivity observed upon transition to bcc would seem to indicate that the bcc phase is probably denser. If this is the case, then the hcp-bcc phase boundary has to have a negative slope.

Erbium, Thulium, and Lutetium

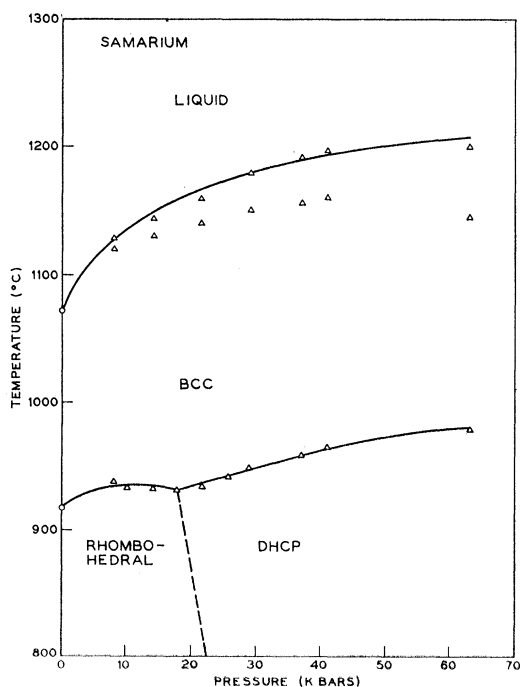Fusion experiments were carried out on Er, Tm, and Lu at about 8 kbar. No thermal arrest signal other than

FIG. 4. Phase diagram of samarium.

[15] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 83, 1 (1954).
[16] H. D. Stromberg and D. R. Stephens, J. Phys. Chem. Solids 25, 1015 (1964).
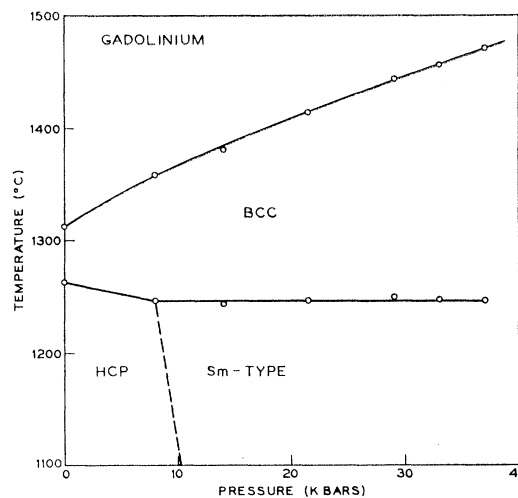[17] D. B. McWhan and A. L. Stevens, preceding paper 139, A682 (1965).

FIG. 5. Phase diagram of gadolinium.

melting was detected. However, this would not rule out by itself the existence of a transformation to the bcc, if such a transformation was within 5° of the melting point. It is to be noted, however, in this connection that Spedding et al.[14] did not observe any abrupt resistance change near the melting temperature for Er and Lu. Miller and Daane[18] conclude from a study of the alloying behavior of rare-earth metals with Mg that a high-temperature bcc allotrope should exist for all the rare-earth metals. But the present experiments on the fusion behavior would seem to indicate (see Discussion) that a transformation to the bcc is probably not present.

The thermodynamic data of interest are collected in Table III.[19–21] The entropies for the bcc transformations and fusion were obtained from Refs. 19, 20, and 21.

DISCUSSION

Fusion Behavior

Most of the rare-earth metals undergo a transformation to the bcc structure before melting and thus offer a series whose fusion properties can be compared. In Fig. 7, the initial melting slopes of the members have been plotted against atomic number. Although this plot has some features in common with the plot of atomic radius versus atomic number,[19] it shows some striking deviations. The atomic radius smoothly decreases with atomic number except at Eu and Yb, the anomalous properties of which are attributed to their divalent state. In Fig. 7 it is seen that La, Nd, Gd, and

[18] A. E. Miller and A. H. Daane, Trans. AIME 230, 568 (1964).
[19] Rare Earth Alloys, edited by K. A. Gschneidner, Jr. (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1961), p. 24, 4, 14.
[20] The Rare Earths, edited by F. H. Spedding and A. H. Daane (John Wiley & Sons Inc., New York, 1961), p. 185.
[21] K. A. Gschneidner, Jr., A. H. Daane, and D. H. Dennison, Ames Laboratory Annual Summary Research Report No. IS-900, M-20, 1964 (unpublished).

TABLE III. Thermodynamic data from Refs. 19, 20, and 21. S-S = transformation to bcc structure; S-L = melting.

R.E. metal	MP (°C)	Transformation temperature to bcc (°C)	ΔS/mol.		$dT/dP°$/kbar		ΔV/mol.		Triple-point coordinates
			S-S	S-L	S-S	S-L	S-S	S-L	
La	920	864	0.67	1.34	5	2.5	0.14	0.14	fcc-bcc-Liq. 19 kbar 965°C
Ce	797	725	0.70	1.157	−1.4	−4.7	−0.04	−0.22	See Ref. 2
Pr	935	792	0.71	1.365	~2[a]	~0.1	0.06	0.005	fcc-bcc-Liq, dhcp-fcc-bcc 48 kbar 938°C, ~8 kbar ~810°C
Nd	1024	862	0.63	1.314	~2[a]	3.5	0.05	0.19	dhcp-fcc-bcc 21 kbar 890°C
Sm	1072	917	0.625	1.53	~3[b]	11.5	0.08	0.72	Rhomb.-dhcp-bcc 18 kbar 930°C
Eu	826			2.23		15		1.39	
Gd	1312	1264	0.607	1.53	~−1.5[c]	6.5	−0.04	0.41	hcp-Sm-type-bcc 8 kbar 1245°C
Tb	1356	1317	0.80	1.56	~0.4[c]	9		0.61	
Dy	1407	1392	...	2.04	~5.0[c]	~12		0.93	
Ho	1461	1442	...	2.25	~12[c]	~15		1.4	
Er	1497			2.67		~15		1.66	
Tm	1545			2.31		~12		1.25	
Yb	824	798	0.396	1.64	−16	19	−0.26	1.26	
Lu	1652			1.71		~8.5		0.64	

[a] dhcp → bcc.
[b] rhombohedral → bcc.
[c] hcp → bcc.

Lu fall on a line, designated trivalent, and Eu and Yb on another, designated divalent. While all the heavier rare earths and Sm fall above the line labeled trivalent, Ce and Pr are below it. Except for Ce the melting slopes of all the rare-earth elements are positive.

The melting slope is given by the Clapeyron equation, $dT/dP = \Delta V/\Delta S$. In the case of Ce it was shown[2] that the ΔV term was dominant in determining the trajectory of the fusion curve and the broad minimum reflected a progressive density increase in the neighboring fcc phase, caused by a continuous transformation from γ to α Ce ($4f$-$5d$ electron promotion). To account for the high density of liquid Ce relative to the bcc and fcc phases, it was suggested that the atoms in the liquid underwent a transition to the tetravalent state due to the same electron promotion. Thus it became evident that the valence state of Ce in the liquid as well as in the solid changed with pressure and temperature. This suggests that in interpreting the high-pressure, high-temperature behavior of the rare-earth metals, the valence state of the atoms in the liquid as well as in the solid is an important factor, as this would influence the ΔV term: the atomic size for the rare-earth elements depends on the valency and increases in the sequence tetravalent < trivalent < divalent. If the atoms in the liquid have a lower valency compared to the atoms in the solid, ΔV of fusion would be positive and larger than usual. In the opposite situation, ΔV of fusion would be
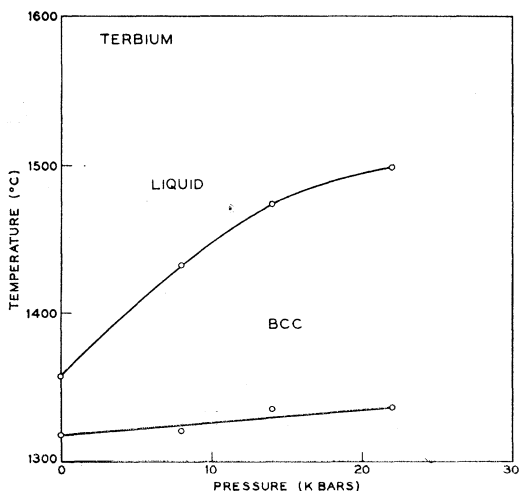

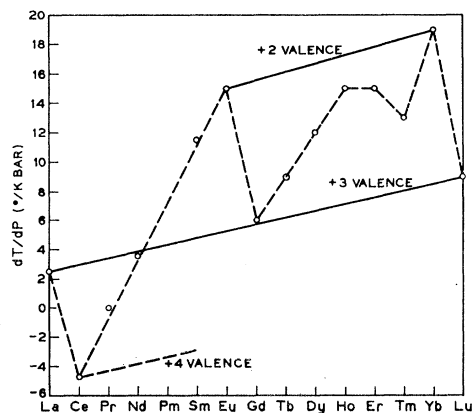FIG. 6. Phase diagram of terbium.

FIG. 7. The initial melting slopes of the R.E. metals plotted against atomic number.

negative and consequently the melting slope would also be negative (as in the example of Ce). Another factor to be reckoned with is the magnetic contribution to the entropy, especially important in the case of heavier rare earths, but at high temperature this is probably negligibly small.

For the rare-earth series, it is experimentally established that the divalent metals Eu and Yb[1] have the highest dT/dP of fusion (see Table III and Fig. 7). In these, both the solid and the liquid would be expected to maintain divalency because the half-filled and completely filled $4f$ states are preferred. For the same reason Gd and Lu would maintain trivalency both in the solid and in the liquid state. Lanthanum would behave accordingly, since it would prefer an empty $4f$ shell. Indeed, it has been shown that the latter elements are trivalent even in the gaseous state (neutral atoms),[22] while Eu and Yb retain their divalency. Therefore the line connecting Eu and Yb (see Fig. 7) has been labeled divalent and the line connecting La, Gd, and Lu trivalent. It is suggested that the rare-earth elements falling above the trivalent line assume partial divalent character in the liquid state and possibly also in the solid bcc phase, while those below the line assume a tetravalent character in the liquid, the latter situation being exemplified in Ce. It should be pointed out that the above suggestion receives some support from the valence state observed for the gaseous neutral atoms of the rare-earth elements. With the exception of La, Gd, and Lu, the ground-state electronic configurations[22] have been found to be $4f^{1-14}5d^06s^2$, implying that they are divalent. It is not therefore improbable that in the liquid the atoms assume a partial divalent character. On the basis of this picture we discuss the results.

The fusion behavior of Ce has already been discussed. To explain the very small positive initial slope of Pr, indicative of a vanishingly small ΔV of fusion, it is suggested that there is a decrease in the atomic size in the liquid, due to partial excitation of the $4f$ electron into $5d$; this would compensate for the usual expansion on melting. Neodymium falls on the trivalent line and apparently adheres to trivalency in both the solid and the liquid. A melting slope of 7°/kbar is predicted for Pm. Samarium has a dT/dP well above the trivalent line and may therefore be expected to have a large divalent character. A divalent oxidation state is easily formed in the case of Sm, and this indicates that the above situation is a plausible one. The sudden drop in dT/dP in passing from Eu to Gd and from Yb to Lu is due to the strict adherence of Gd and Lu to trivalency irrespective of the state of aggregation, temperature, and pressure. The partial divalent character postulated for those members which lie above the trivalent line apparently increases in going from Nd to Sm and from Gd to Ho or Er. We have no explanation to offer for this tendency in the heavier rare earths, although in the

case of Sm there is some support. We have also not explained why there is a reversal of trend commencing at Er. It may be noted that Er and Tm do not in all probability undergo a transformation to the bcc structure before melting.

The alkali metals,[23] all of which crystallize in the bcc structure, offer a series for a comparative discussion. While their melting slopes decrease with increasing melting point (from Cs to Li), the general trend for the rare earths, leaving out Eu and Yb, is an increase in the slope with increasing melting point. In the alkali metals the increasing slope[23] is strikingly related to increasing compressibility; Cs, which is the most highly compressible of all, has the highest initial slope. This is also true for the rare earths, as far as can be judged from available data.[15,24] Eu and Yb, which are the most compressible, have the highest melting slope. In view of this, the large positive initial slopes of the members, especially those which lie above the trivalent line, suggests that they may be quite compressible. Apparently in the bcc phase and at high temperatures most of the rare-earth metals are quite soft and have compressibilities much larger than the room-temperature measurements indicate. Because of the lack of information on compressibility of the rare-earth metals in the bcc phase, a quantitative comparison with the available melting theories could not be made, such as has been done in the case of alkali metals.[25]

Solid-Solid Transformations

Pressure-induced phase transformations in the rare-earth metals are found to be in the sequence hcp → Sm type → dhcp → fcc.[11] These structures differ only in the stacking of the atomic layers, and are in the order of increasing cubicity; in Sm-type ($hhchhc\cdots$) and in dhcp ($hchc\cdots$) one-third and one-half the layers, respectively, have cubic close packing and the rest have hexagonal close packing. It was suggested in the case of Gd[12] that the transformation to Sm-type structure might be connected with an increase in c/a. This ratio is found to be distinctly higher for the lighter rare earths than for Gd to Lu. McWhan and Stevens[17] find that in Gd, and also in Tb, Dy, and Ho, the c/a ratio increases with pressure. Rare-earth alloys crystallizing in the Sm-type structure have c/a ratios (when normalized by dividing by 4.5) very close to 1.604±4. This suggests that a rare-earth metal with hcp structure might be expected to transform to the Sm-type structure under pressure when this value is realized for c/a. Spedding et al.[14] report that with temperature also the c/a ratio increases, and the transformation to bcc structure is observed in Y, Gd, Tb, and Ho when the ratio is between 1.600 and 1.602. However, at high pressure,

[22] A. Y. Cabezas, I. Lindgren, and R. Marrus, Phys. Rev. 122, 1796 (1961).

[23] R. C. Newton, A. Jayaraman, and G. C. Kennedy, J. Geophys. Res. 67, 2559 (1962).

[24] D. R. Stephens, J. Phys. Chem. Solids 25, 423 (1964).

[25] J. J. Gilvarry, Phys. Rev. 102, 308 (1956).

the atomic volume would be smaller, whereas at high temperature it would be higher, and the two situations are therefore different.

The phase diagrams (see La to Gd) reflect the relative stability of the hcp, Sm-type, dhcp, and fcc phases under pressure. The stability field of the bcc phase progressively increases from La upwards in the series, with the exception of Ce, for which this field is closed at relatively low pressure. As one moves from La to Gd the crystalline phases step in into the *P-T* field in the order fcc → dhcp → Sm-type → hcp; pressure of course

favors the reverse order. It appears that to get all the possible phases of the sequence for a hcp R.E. metal one has to push higher in pressure. Thus in Gd all four may be expected. McWhan and Stevens's[17] magnetic work on Gd would seem to indicate the appearance of another phase above 50 kbar, which might be the dhcp phase.

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Three-Quantum Annihilation of Positrons in Metals and Insulators

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The three-quantum decay of positrons annihilating in some metals and in some insulators was investigated by using a triple coincidence method. Relative measurements were made by comparing the three-quantum yield in each substance with that of aluminum. Small differences between the three-quantum yields of various metals were found: in Pb, where this effect appears to be the largest, the relative yield is P/P_0 $= 1.16 \pm 0.03$. At present any simple attempt to explain this result is unsuccessful. From the relative three-quantum rates measured in insulators, and on the basis of a simple model, the following information was obtained: The contribution to three-quantum production in insulators due to the positronium atom arises only from the orthostate decaying with a partial lifetime τ_3 equal to that in free space $(\tau_3 = 1.39 \times 10^{-7}$ sec). No evidence was found of three-quantum production arising from interaction of the positronium with matter. The remaining three-quantum annihilations occur with the same yield characteristic of positrons in Al $(P_f/P_0 = 1.00 \pm 0.05)$. From the same measurements in insulators, the yield in Al is $P_0 = (2.64 \pm 0.08)10^{-3}$, in good agreement with the value predicted by Ore and Powell (2.70×10^{-3}).

I. INTRODUCTION

THE time spectrum of the annihilation radiation of positrons in metals is known to be simple according to the results of most of the investigations carried out. In a few cases, however, the decay curve appears to be complex with about 5% of the events having a mean life approximately 5×10^{-10} sec.[1,2,3,4] Weisberg[4] has recently pointed out that the "tail" intensity can depend on sample-preparation techniques, i.e., that at least part of it can arise from annihilation in the source or in impure surface layers of the metal. Any attempt to explain the existence of such a tail meets serious difficulties owing to the fact that the electron-positron system in a metal possesses no "bound state" analogous to positronium, as recently shown by Held and Kahana.[5]

In some solid insulators the time spectrum of the annihilation radiation of positrons is known to be complex, as was shown for the first time by Bell and

Graham.[6] The experiments show that at least two distinct components are present with lifetimes of a few times 10^{-10} sec (τ_1) and a few times 10^{-9} sec (τ_2). To the prompt mode of decay there certainly contribute: (1) those positrons which, having survived the slowing-down process, miss the ore gap and annihilate in the free state with emission of two or three quanta; (2) those positrons which have become bound to an electron in parapositronium (this is one-third of the τ_2 percentage). The τ_2 component is due to the formation and decay of orthopositronium. It should be remembered that in parapositronium the positron annihilates with its own electron into two quanta with a mean life of 1.25×10^{-10} sec; this process is forbidden in orthopositronium, which in free space decays only with emission of three quanta $(\tau_3 = 1.39 \times 10^{-7}$ sec). In matter, however, another process prevails over the three-quantum decay, i.e., the annihilation of the positron with an electron of the surrounding molecules, whose spin state relative to it is a singlet ("pick-off" annihilation).

The relative yield of three-quantum events from positrons annihilating when free is equal to 1/372

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