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The Relationship between Atomic Radii in Close-packed and Body-centered Cubic Structures

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Data on transitions between the body-centered cubic structure and either the cubic or hexagonal close-packed structure for sixteen elements have been examined, and it is found that the equation $R(1) - \tilde{R}(n) = 0.300 \log n$ does not satisfactorily account for the observed interatomic distances. On the other hand, the ratios R(12)/R(8)between the atomic radii in the two structures all lie quite close to the value of 1.029 expected if the volume change on transition is zero.

Introduction

R(1)

In a now classic paper Pauling¹ proposed the equation

$$- R(n) = 0.300 \log n \tag{1}$$

to relate the univalent radius, R(1), of an atom to the radius when the valence is n. This relation was not used, however, to calculate the atomic radius appropriate to coördination number 12, *i.e.*, for cubic or hexagonal close-packed structures, from those observed in body-centered cubic structures, where the coördination number is 8, because the differences between bodycentered cubic and close-packed radii for Fe, Ti, Zr, and Tl, which crystallize with both structures, did not fit the equation. Instead, an empirical curve based on data obtained from these four metals was given, from which the values of $\Delta R = R(12) - R(8)$ as a function of R(8) could be read. The assumptions made in calculating ΔR with (1) are that the valence is the same in both structures, and that while only the 12 nearest neighbors need be considered in the close-packed structures, the bond forming of both the 8 nearest and 6 next nearest neighbors in the body-centered cubic structures must be taken into account. Somewhat later Thewlis² pointed out that the points used to obtain the empirical curve were based on data at different temperatures in the case of Ti, Zr and Tl and on an unreliable extrapolated value³ in the case of Fe, and stated that when allowance for thermal expansion was made, little or no modification of eq. 1 was needed. However, the extrapolations used by Thewlis are also unreliable, inasmuch as the thermal expansion coefficients not only were apparently assumed constant, but also the extrapolations were very large, *i.e.*, from 950°, 900°, 867° and 262° to room temperature. Moreover, there are now available data on twelve more elements which crystallize with both structures. Accordingly, it is possible to make a more extensive test of eq. 1 than has been done heretofore.

Lattice Constants

Some of the numerical data in this section may be found in Pearson,⁴ but the original literature citations are also given. Lattice constants are in Angstrom units throughout, the factor 1.00202 having been used to convert from kX where necessary. The abbreviations bcc, ccp and hcp are used to denote the body-centered cubic, cubic close-packed and hexagonal close-packed structures, respectively. Greek letter designations have not been used, as their use is sometimes confusing.

Helium-3 exhibits complicated phase behavior.⁵ The equations of Grilly and Mills⁶ give the following quantifies relative to the bcc \rightarrow hcp transition at 3.148°K.: p = 140.45 kg. cm.⁻², ΔV (solid_{bcc} \rightarrow liquid) = 0.767 cm.³/mole, ΔV (solid_{hep} \rightarrow liquid) = 0.897

(3) Strukturbericht, 4, 228 (1936).

- (4) W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys," Pergamon Press, London, 1958.
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cm.³/mole, $V_{\text{liquid}} = 19.718$ cm.³/mole. From these we obtain $a_0 = 3.978$ Å. for the bcc form and (assuming $c_0/a_0 = 1.634$, the same value observed⁵ at a higher pressure) $a_0 = 3.535$, $c_0 = 5.776$ Å. for the hcp form. These data refer to the triple point bcc-hcp-liquid. The other extreme of the transition line between bcc and hep occurs at 102 kg. cm.-2 and 0°K., at which point it was found that ΔV (solid_{bcc} \rightarrow liquid) = ΔV $(\text{solid}_{hep} \rightarrow \text{liquid}) = 0.840 \text{ cm.}^3/\text{mole}, V_{\text{liquid}} = 20.900 \text{ cm.}^3/\text{mole}.$ These values give, for the bcc form $a_0 = 4.054$ Å., and for the hep form $a_0 = 3.612$, c_0 = 5.898 Å.

Helium-4 also exhibits complex phase behavior,⁵ and different from that of helium-3. The pVT measurements of Grilly and Mills⁷ give, at 1.73° K. and 29.01 atm., molar volumes of 20.928 cm.3 for the bcc form and 20.737 cm.³ for the hcp form. The resulting lattice constants are $a_0 = 4.111$ Å. for bcc, and (assuming $c_0/a_0 = 1.629$, the same value observed⁸ at a slightly higher pressure) $a_0 = 3.655$, $c_0 = 5.954$ Å. for hcp.

Lithium is bcc at room temperature and below, but at low temperatures both the ccp and hcp forms also have been observed. The transition bcc \rightarrow hcp, on cooling, is spontaneous and partial at about 78°K. The partial transition bcc \rightarrow ccp is induced by cold working at 78°K. Observed lattice constants at 78°K. are: for bcc,⁹ $a_0 = 3.4831$ Å.; for ccp,⁹ $a_0 = 4.379$ Å.; for hcp, ${}^{10}a_0 = 3.104, c_0 = 5.081$ Å.

Sodium undergoes a spontaneous, partial transformation from bcc to hcp on cooling below 36° K. At 5° K. the lattice constants¹⁰ are $a_0 = 4.225$ Å. for bcc and a_0 $= 3.767, c_0 = 6.154$ Å. for hcp.

Calcium of sufficiently high purity undergoes one transition between room temperature and the melting point, transforming at about 464° from ccp to bcc. The lattice constant of the bcc form¹¹ at 467° is 4.480 Å. The observed lattice constant of the ccp form¹¹ at 26° of 5.5884 Å. together with the average thermal expansion coefficient^{11,12} of 22.3 \times 10⁻⁶ between 0° and 371° give 5.644 A. for the lattice constant at 467°

Strontium, which is ccp at room temperature, changes to the hcp structure at about 215°13 or 235°,14 then at about 535°14 or 605°13 to a bcc form which persists up to the melting point. The lattice constant at 25° is 6.0849 Å. The lattice constants of the two high temperature forms have been measured only approximately, and at only one temperature each, 366° apart. However, the dilatometric data14 may be used to calculate the appropriate crystal structure data: between 0° and $53\overline{5}^{\circ}$ the linear expansion is 11.6×10^{-3} , and at the

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⁽⁸⁾ A. F. Schuch and R. L. Mills, Phys. Rev. Letters, 8, 469 (1962).

⁽⁹⁾ E. A. Owen and G. I. Williams, Proc. Phys. Soc., A67, 895 (1954).

⁽¹⁰⁾ C. S. Barrett, Acta Cryst., 9, 671 (1956). The values $a_0 = 3.111$ and $c_0 = 5.093$ Å, given by Barrett have been adjusted to take account of the fact that he used the value 3.491 Å. for the lattice constant of bcc Li as an internal standard in his study of the hcp form.

⁽¹¹⁾ B. T. Bernstein and J. F. Smith, Acta Cryst., 12, 419 (1959).

hcp \rightarrow bcc transition there is a linear contraction of 0.9×10^{-3} . These data, combined with the ccp lattice constant quoted above, give, for the hcp form (assuming $c_0/a_0 = 1.636$, the value observed¹³ at 248°) $a_0 = 4.347$, $c_0 = 7.112$ Å., and $a_0 = 4.879$ Å. for the bcc form, both at 535°. (These values are in fair agreement with the directly measured values¹³ of $a_0 = 4.32$, c_0 = 7.06 Å, for hep at 248° and $a_0 = 4.85$ Å, for bee at 614°.)

Lanthanum¹⁵ is ccp at room temperature, and an hcp form (with a doubled c_0) may coexist with this up to 292°. The atomic volume of the hcp form is less than 0.5% larger than that of the ccp form. At 868° there is a transition $ccp \rightarrow bcc$. The lattice constant for the bcc form is 4.25 Å. at 881°. Data for the ccp form obtained in the range of 21° to 598° extrapolate to a lattice constant of 5.341 Å. at 881°. The extrapolation function includes terms in t and t^2 .

Cerium¹⁵ is ccp at room temperature and bcc above 730° . At 742° the bcc lattice constant is 4.11 Å. Data for the ccp form from the range 13° to 619° extrapolate to a lattice constant of 5.187 Å. at 742°. The extrapolation function includes terms in t, t^2 and t^3 .

Praseodymium¹⁵ is double-hcp at room temperature and transforms to the bcc form at 798° with lattice constant 4.13 Å. at 814°. Data for the hexagonal form from the range 22° to 449° extrapolate to the lattice constants $a_0 = 3.684$, $c_0 = 11.936$ Å. at 814°. The extrapolation functions are linear in t.

Neodymium¹⁵ is also double-hcp at room temperature and transforms to the bcc form at 868°. The lattice constant is 4.13 Å. at 882°. Data for the hexagonal form from the range 20° to 696° extrapolate to $a_0 = 3.688, c_0 = 11.956$ Å. at 882°. The extrapolation functions contain terms in t, t^2 and t^3 .

Ytterbium¹⁵ is ccp at room temperature. Atmospheric impurities stabilize an hcp structure above 260° which transforms to a bcc form at 720°, at which temperature the lattice constant is 4.44 Å. Data for the ccp form from 23° to 598° extrapolate to $a_0 =$ 5.596 Å. at 720°. The extrapolation function includes terms in t, t^2 and t^3 . The atomic volume of the hcp form is larger than that of the ccp form by 0.8% at about 260°, the difference gradually decreasing to 0.3% at about 410°.

Thallium transforms from hep to bee at about 230°. At 262° the lattice constant of the bcc form¹⁶ is 3.882 Å. Thermal data on the hcp form¹⁷ at 18°, 102° and 192°

extrapolate to $a_0 = 3.489$, $c_0 = 5.541$ Å. at 262°. **Titanium** is hep at 25°, with $a_0 = 2.9504$ Å., $c_6 = 4.6833$ Å.¹⁸ At about 882°, there is a transition hcp \rightarrow bcc, but the thermal expansion data on the hcp form are unreliable¹⁹ because of contamination above 600° by Si, O and N, the lattice constants above room temperature showing considerable scatter. Extrapolation to 100% of Ti for the bcc phases of Ti-Cr, 20 Ti-Fe, 21,22 Ti-Mn, 23 Ti-Mo 24 and Ti-Zr, 25 all at room temperature, gives the respective values $a_0 = 3.284$, 3.296, 3.281, 3.286 and 3.287 Å.; average $a_0 = 3.287$ Å., a.d. = 0.004 Å. The respective observed composition

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TABLE I EXTRAPOLATION OF LATTICE CONSTANTS

	-Ti-Cr-			-Ti-Fe-			-Ti-Mo-	
Atom			Atom			Atom		
%			%			%		
of Cr,	<u> </u>	Å.——	of Fe,	<i>—a</i> ₀ ,	Å.——	of Mo,	<u> </u>	, Å.—
Þ	Obsd.	Calcd.	Þ	Obsd.	Calcd.	Þ	Obsd.	Calcd.
6	3.260	3,261	4.40	3.255	3.257	11.5	3.250	3.251
8	3.254	3.253	5,00	3.249	3.253	18.0	3.237	3.234
10	3.245	3.245	5.2	3.260	3.251	33.5	3,198	3,199
12	3.236	3.237	6.68	3.237	3.239	42.5	3.184	3.181
14	3.230	3.230	12.0	3.210	3.202	53.5	3.165	3.165
16	3.222	3,222	12.07	3.195	3.201	66.5	3.149	3.150
$a_0 =$	3.284 -	-	13.86	3.186	3.191	82.0	3.142	3.141
3.8	85×10^{10})-3 p	14.5	3.195	3.187	100.0	3,140	3.140
a.d	= 0.00	01 Å.	15.39	3.175	3.183	$a_0 = 3$	3.286 -	$_{3,2}$ \times
			16.5	3.180	3.179	10-3	p + 1	$1.74 \times$
			20.2	3.160	3.161	10-5	p^2	,
			$a_0 = 3.2$	296 - 9	.5 X	a.c	1. = 0.00	1 Å.
			10-3 1	+1.4	×			
			10-4 1	²				
			a.d.	= 0.00	95 A.			
	Ti–N	Ín		Ti-Zi	r		Tl	
Atom			Atom					
%			%					
of Mn	,	·ao, Å.——	of Zr,	<i>a</i>), Å.——	t,	<u> </u>	Å.——
Þ	Obse	I. Caled	l. p	Obsd.	Calcd.	°C.	Obsd.	Calcd.
5.5	3.24	2 3.24	6 30	3.377	3.377	18	3,456	3,456
6.2	3.24	4 3,24	2 40	3.407	3.407	102	3.469	3.469
8.8	3.23	3 3,22	7 50	3.437	3,437	192	3,481	3,481
12.0	3.21	3 3.21	3 60	3.467	3.467	262		3.489
13.4	3.20	7 3.20	7 70	3.497	3,497	$a_0 =$	3.453 -	- 17 ×
13,4	3.20	3 3.20	$7 a_0 =$	3.287 -	+ 0.003⊅	10 -5 t	$-12 \times$	10 -8/2
18.1	3.19	9 3.19	0				co,	A.—
18.1	3.18	3 3.19	0			<i>ι</i> , °C.	Obsd.	Calcd.
$a_0 =$	3.281 -	- 7 ×				18	5.530	5.530
10	-* p + :	1.1×10^{-1}	-4 p2			102	5.535	5.535
а	d. = 0	0.004 Å.				192	5.539	5.539
						262		5.541
						c0 =	5.529	+ 7 ×
						10-	°t - 87	×
						10-	.815	

ranges, in atom % Ti, are 84–94%, 79.8–95.6%, 81.9–94.5%, 0–88.5% and 30 to 70%. The first and last extrapolations are linear, the other three quadratic.

Zirconium undergoes a transition hep \rightarrow bee at about 865°. At 862° the observed²⁶ lattice constant of the bcc phase is 3.6090 Å., while those calculated²⁶ for the hep form by the use of quadratic extrapolation of data collected between 10° and 579° are $a_0 = 3.2491$, $c_0 = 5.2010 \,\mathrm{A}.$

Macroscopic measurements²⁷ give a volume decrease of 0.66% at the transition; this result, when combined with the foregoing hep lattice constants, gives 3.615 Å. for a_0 of the bcc form.

At 25° the lattice constants of the hcp phase²⁸ are $a_0 = 3.2312, c_0 = 5.1477$ Å. The bcc form is not stable at room temperature, but extrapolation of data from bec Zr-Ti²⁵ (30 to 70 atom % Zr) and bec Zr-U²⁹ (40 to 90 atom % Zr) to 100% of Zr both give 3.587 Å. for the value of a_0 for bcc Zr at room temperature.

Thorium transforms at about 1450° from ccp to bcc. The respective lattice constants³⁰ at that temperature are 5.180 and 4.11 Å.

Manganese transforms from ccp to bcc at about 1130°. The respective lattice constants are³¹ 3.868 and 3.080 Å. The dilatometrically observed³² volume change at the transition is +0.90%; this figure, together with the above ccp lattice constant, gives the value 3.079 Å. for a_0 of the bcc phase.

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∆v = 0

R(I2)- R(8) .05 R(1)-R(n) = 0.300 log n .04 03 directly observed via observed volume change at transition 02 via thermal expansion of low temperature form Ο via alloys .01 С 1.20 140 1.60 1.80 2.00 2.20 2.40 R(8)

Fig. 1.—The relation between $\Delta R = R(12) - R(8)$ and R(8).

Iron undergoes a transition bcc \rightarrow ccp at 916°. At that temperature, the respective lattice constants³³ are 2.9044 and 3.6468 Å. At 1388° there is a second transition ccp \rightarrow bcc, the lattice constants³³ being 3.6869 and 2.9315 Å.

Additional numerical data involving some of the extrapolated data are presented in Table I.

Discussion

The lattice constants in the foregoing section may be used to calculate the atomic radii in the various allotropes. The results are presented in Table II. Values of ΔR vs. R(8) are shown in Fig. 1, in which it may be seen that while the revised data for Fe and Ti are in satisfactory agreement with eq. 1, those for Tl and Zr are not. Moreover, the data for the twelve additional elements show rather poor agreement with the predictions of eq. 1, especially at the larger values of R(8). It would thus appear that eq. 1 is not appropriate for calculating the values of R(12) from the directly observed values of R(8) for those elements which crystallize only with the bcc structure. This result also raises doubt as to whether eq. 1 should therefore be used, as has been widely done, in the interpretation of interatomic distances in intermetallic compounds.

It is interesting that the relation

$$R(12) = kR(8)$$
 (2)

with $k = 6^{1/2}2^{1/3}/3 = 1.029$ reproduces the observed data satisfactorily. This function results from the assumption that transition from the close-packed struc-

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			TABLE	II		
Атоміс	Radii	IN	CLOSE-PACKED	(R12)	AND	BODY-CENTERED
CUBIC (R8) STRUCTURES						

				$R(12)^a$	
	R(8)	R(12)	ΔR^a	R(8)	Remarks
He-3	1.723	1.768	0.045	1.026	At 3.148°K., from pVT data
He-3	1.755	1.806	.051	1.029	At 0°K., from pVT data
He-4	1.780	1.826	.046	1.026	At 1.73°K., from pVT data
Li	1.508	1.548	.040	1.027	At 78°K., from ccp \rightarrow bcc
Li	1.508	1.553	.045	1.030	At 78°K., from hep \rightarrow bee
Na	1.830	1.884	. 054	1.030	At 5°K.
Ca	1.940	1.995	.055	1.029	At 467 °C., $R(12)$ from thermal data
Sr	2.113	2.175	.062	1.029	At 535°C., via thermal data
La	1 840	1.888	.048	1.026	At 881°C., $R(12)$ from thermal data
Ce	1.780	1.834	.054	1.030	At 742°C., $R(12)$ from thermal data
Pr	1.788	1.837	.049	1.027	At 814°C., $R(12)$ from thermal data
Nd	1.788	1.839	.051	1.029	At 882°C., $R(12)$ from thermal data
YЬ	1.923	1,979	.056	1.029	At 720°C., $R(12)$ from thermal data
T1	1.681	1.729	.048	1.028	At 262°C., $R(12)$ from thermal data
Ti	1.423	1.461	.038	1.027	At room temperature, $R(8)$ from al-
					loys
Zr	1.563	1.614	.051	1.033	At 862°C., $R(12)$ from thermal data
Zr	1.553	1.602	.049	1.032	At room temperature, $R(8)$ from al-
					loys
Zr	1.565	1.614	.049	1.031	At 862°C., from obsd. ΔV , hep \rightarrow bee
Th	1.780	1.831	.052	1.029	At 1450°C.
Mn	1.334	1.368	. 034	1.025	At 1130°C.
Mn	1.333	1.368	. 034	1.026	At ca. 1130°C., from obsd. ΔV
Fe	1.258	1.289	. 032	1.025	At 916°C.
Fe	1.269	1.303	. 034	1.027	At 1388°C.

^a These quantities were calculated from the lattice constants given in the text in order to avoid rounding off errors.

tures to the bcc structure occurs with zero change in volume. For ΔV of plus and minus 1%, the values of k are 1.032 and 1.025, respectively; all except one of the points of Fig. 1 lie within these limits. This near constancy of the concentration of electrons implies that the total bond forming power per atom, *i.e.*, the valence, is essentially unchanged during the transition. It is noteworthy that the $\Delta V = 0$ approximation and eq. 2 are valid for elements with widely differing properties, *i.e.*, from the alkali metals to the transition metals and even a group 0 element, helium, and under widely different conditions, including the temperatures at which the transitions take place, at room temperature (by extrapolation) and in certain alloys (also by extrapolation).

In the foregoing discussion no assumptions were made concerning the valences of atoms and their dependence on interatomic distances. The gradual divergence from the predictions of eq. 1 of the observed values of ΔR as R(8) increases suggests that although the equation may be useful in the consideration of distances between the smaller atoms, some modification will be required in the case of the larger atoms, but the development of such a relation is outside the scope of the present paper.

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