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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 $R(1) - R(n) = 0.300 \log n$ 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

In a now classic paper Pauling¹ proposed the equation

$$R(1) - R(n) = 0.300 \log n \quad (1)$$

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 coordination number 12, *i.e.*, for cubic or hexagonal close-packed structures, from those observed in body-centered cubic structures, where the coordination number is 8, because the differences between body-centered 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 Ångstrom 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 quantities relative to the bcc \rightarrow hcp transition at 3.148°K.: $p = 140.45 \text{ kg. cm.}^{-2}$, $\Delta V (\text{solid}_{\text{bcc}} \rightarrow \text{liquid}) = 0.767 \text{ cm.}^3/\text{mole}$, $\Delta V (\text{solid}_{\text{hcp}} \rightarrow \text{liquid}) = 0.897$

$\text{cm.}^3/\text{mole}$, $V_{\text{liquid}} = 19.718 \text{ cm.}^3/\text{mole}$. From these we obtain $a_0 = 3.978 \text{ Å.}$ for the bcc form and (assuming $c_0/a_0 = 1.634$, the same value observed⁵ at a higher pressure) $a_0 = 3.535$, $c_0 = 5.776 \text{ Å.}$ for the hcp form. These data refer to the triple point bcc-hcp-liquid. The other extreme of the transition line between bcc and hcp occurs at 102 kg. cm.^{-2} and 0°K., at which point it was found that $\Delta V (\text{solid}_{\text{bcc}} \rightarrow \text{liquid}) = \Delta V (\text{solid}_{\text{hcp}} \rightarrow \text{liquid}) = 0.840 \text{ cm.}^3/\text{mole}$, $V_{\text{liquid}} = 20.900 \text{ cm.}^3/\text{mole}$. These values give, for the bcc form $a_0 = 4.054 \text{ Å.}$, and for the hcp form $a_0 = 3.612$, $c_0 = 5.898 \text{ Å.}$

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 $a_0 = 4.111 \text{ Å.}$ for bcc, and (assuming $c_0/a_0 = 1.629$, the same value observed⁸ at a slightly higher pressure) $a_0 = 3.655$, $c_0 = 5.954 \text{ Å.}$ 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 $a_0 = 3.4831 \text{ Å.}$; for ccp,⁹ $a_0 = 4.379 \text{ Å.}$; for hcp,¹⁰ $a_0 = 3.104$, $c_0 = 5.081 \text{ Å.}$

Sodium undergoes a spontaneous, partial transformation from bcc to hcp on cooling below 36°K. At 5°K. the lattice constants¹⁰ are $a_0 = 4.225 \text{ Å.}$ for bcc and $a_0 = 3.767$, $c_0 = 6.154 \text{ Å.}$ 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 22.3×10^{-6} between 0° and 371° give 5.644 Å. 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 535° the linear expansion is 11.6×10^{-3} , and at the

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(2) J. Thewlis, *ibid.*, **75**, 2279 (1953).

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(4) W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys," Pergamon Press, London, 1958.

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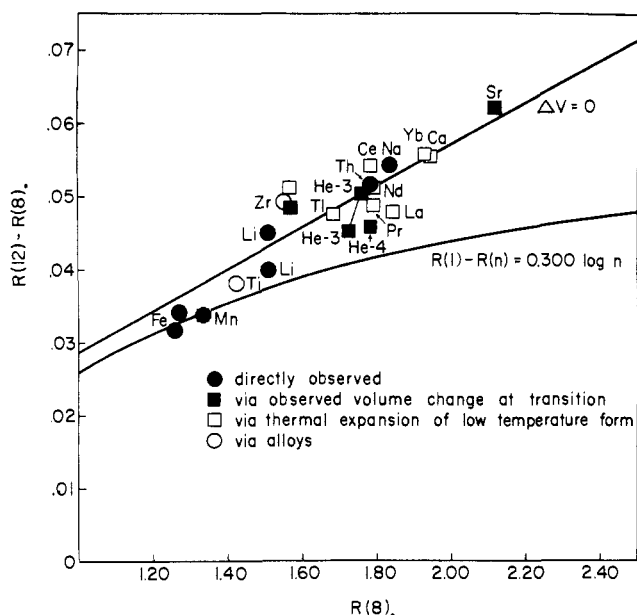


Fig. 1.—The relation between $\Delta R = R(12) - R(8)$ and $R(8)$.

Iron undergoes a transition $\text{bcc} \rightarrow \text{ccp}$ at 916° . At that temperature, the respective lattice constants³³ are 2.9044 and 3.6468 Å. At 1388° there is a second transition $\text{ccp} \rightarrow \text{bcc}$, 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 Ti 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

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

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-

(33) Z. S. Basinski, W. Hume-Rothery and A. L. Sutton, *Proc. Roy. Soc. (London)*, **A229**, 459 (1955).

TABLE II
ATOMIC RADII IN CLOSE-PACKED ($R(12)$) AND BODY-CENTERED CUBIC ($R(8)$) STRUCTURES

	$R(8)$	$R(12)$	ΔR^a	$R(12)^a$		Remarks
				$R(8)$		
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 $\text{ccp} \rightarrow \text{bcc}$
Li	1.508	1.553	.045	1.030		At 78°K ., from $\text{hcp} \rightarrow \text{bcc}$
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
Yb	1.923	1.979	.056	1.029		At 720°C ., $R(12)$ from thermal data
Tl	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 alloys
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 alloys
Zr	1.565	1.614	.049	1.031		At 862°C ., from obsd. ΔV , $\text{hcp} \rightarrow \text{bcc}$
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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