

γ -Brasses with *R* cells

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The structures of γ -Cr₅Al₈ and γ -V₅Al₈ have been redetermined by single-crystal methods confirming earlier results. Cr₅Al₈ is rhombohedral, $a = 7.811(3)$ Å, $\alpha = 109.13(2)^\circ$, 26 atoms per cell, space group *R3m* (No. 160), and V₅Al₈ is cubic, $a = 9.234(5)$ Å, 52 atoms per cell, space group *I43m* (No. 217). A hypothesis is put forward to account for the rhombohedral structures of γ -brasses with $\alpha < 90^\circ$ (52-atom cell) in the following systems: Al–Cu, Al–Cr, Al–Mn, Ga–Cr, Ga–Mn and Ga–Fe. The rhombohedral distortion, stabilized by band-structure energy, allows the phases to be stable up to considerably higher electron concentrations than γ -brasses with the cubic structures. Since V₅Al₈ has the cubic rather than the rhombohedral structure, it appears that V must absorb some electrons from the conduction band.

Introduction

γ -Brasses with rhombohedral cells and $\alpha < 90^\circ$ (52-atom cell) have been reported for phases in the Al–Cr, Al–Mn, Al–Cu, Ga–Cr, Ga–Mn and Ga–Fe systems (Meissner & Schubert, 1965; Bradley & Lu, 1937*a*; Westman, 1965). Rhombohedral γ -brass structures with $\alpha > 90^\circ$ have been reported in the Cu–Hg and the Cr–Al systems (Lindahl, Pilotti & Westman, 1968; Lindahl & Westman, 1969).

This paper reports the results of single-crystal structure determinations of a γ -Al–Cr phase (γ_1 or γ_2) undertaken to confirm the earlier X-ray powder structure of Bradley & Lu (1937*b*) and of the γ -Al–V phase undertaken to confirm that it indeed has, as earlier reported from X-ray powder data (Carlson, Kenney & Wilhelm, 1955), a cubic and not a rhombohedral structure.

The γ -brass phases with rhombohedral cells and $\alpha < 90^\circ$ all appear to have valence-electron concentrations in excess of 88 or 89 per 52-atom cell which is normally regarded as the highest electron concentration found for phases with cubic γ -brass structures. We develop a hypothesis which accounts for these phases with *R* cells on the basis that the distortion is stabilized by band-structure energy and that they occur at higher electron concentrations than the cubic γ -phases.

Structure of the rhombohedral Cr₅Al₈ phase

Four Al–Cr phases related to γ -brass were described by Bradley & Lu (1937*a*). γ_1 was said to be a high-temperature phase stable between ~ 1350 and $\sim 980^\circ\text{C}$, whereas γ_2 (at the same composition, Cr₅Al₈, as γ_1) and γ_3 and γ_4 ($\sim \text{Cr}_4\text{Al}_9$) were found to be stable down to room temperature. Bradley & Lu (1937*b*) showed γ_2 to have a rhombohedral γ -brass-like structure and determined the atom positions. However, Knappworst & Nowotny (1941) found a cubic γ -brass structure in alloys containing ~ 31 to 45 at.% Cr (Hansen, 1958).

The single-crystal X-ray structure reported here refers to an alloy with 38.5 at.% Cr prepared from pressed powders of 99.99% pure Al and 99.95% pure Cr by sintering for 6 h at 1000°C, quenching, grinding to powder and re-annealing at 1215°C for 287 h before quenching rapidly in iced brine. A single crystal for the X-ray analysis was selected from the powder. According to the analysis of Bradley & Lu (1937*a*), the crystal whose composition was $\sim \text{Cr}_5\text{Al}_8$ should have been of the γ_1 phase. The close agreement of the results of this analysis with those of Bradley & Lu (1937*b*) suggests either that the structure of γ_1 and γ_2 are very similar, or that our crystals decomposed to γ_2 on quenching.

The crystal examined had an irregular shape which was approximated by a sphere of radius 0.05 mm. Weissenberg X-ray photographs of the crystal aligned along $[1\bar{1}0]$ and precession photographs showed the crystal to be rhombohedral, space group *R3m* (No. 160). The crystal data including pycnometric density

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measurements are summarized in Table 1. The cell constants were determined by a least-squares fit to 2θ values for eight reflexions measured on a General Electric XRD-6 diffractometer using Zr-filtered Mo $K\alpha$ X-radiation ($\lambda = 0.7107 \text{ \AA}$).

According to the description of Bradley & Jones (1933), the γ -brass structure can be considered as built up of clusters of 26 atoms. An inner tetrahedron (*IT*) of four atoms is surrounded by an outer tetrahedron (*OT*), then an octahedron (*OH*) of six atoms, followed finally by a cubo-octahedron (*CO*) of twelve atoms. In the archetype *I* cell structure ($I\bar{4}3m$), the atoms occupy these four crystallographically independent site sets and identical clusters occur at the corners and body centre of the cubic unit cell. In γ -brasses with the *R* cell, these crystallographic site sets are subdivided as indicated in Table 2. Although the data collection and structure refinement were performed on the primitive rhombohedral cell, the body-centred rhombohedral cell with 52 atoms and $\alpha \sim 90^\circ$ allows convenient comparison of atomic coordinates with those in the *I* cell of cubic γ -brasses. The transformations to the body-centred rhombohedral cell are given by

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} \mathbf{a}' \\ \mathbf{b}' \\ \mathbf{c}' \end{pmatrix}$$

where primes refer to the primitive rhombohedral cell.

Intensity data were collected on a General Electric XRD-6 three-circle diffractometer with scintillation counter and pulse-height analyser using Zr-filtered Mo $K\alpha$ radiation. A θ - 2θ scan method [2θ scan range = $\pm(0.9 + 0.3 \tan \theta)^\circ$] was used for reflexions with $2\theta \leq 70^\circ$ in $\frac{1}{3}$ of the hemisphere. Background intensities at the beginning and end of each reflexion scan were measured. A reflexion was considered to be observable

when the background-corrected intensity was greater than $3\sigma(I)$. Absorption corrections were made for a spherical crystal with $\mu R = 0.3$ and Lorentz-polarization corrections were applied to the intensity data with the computer program *DATAPREP* on the University of Waterloo IBM 360/75 computer. The crystallographically equivalent reflexions were averaged and 842 measured reflexions reduced to 263 crystallographically independent observable reflexions and 144 unobservable reflexions.

The full-matrix least-squares program *LSTSQR* was used to refine the structure in terms of the primitive rhombohedral cell, which requires nine crystallographically independent sites as indicated in Table 2. There is one degree of freedom in choosing coordinates for these sites which corresponds to transla-

Table 2. Comparison of crystallographic sites used to describe 26-atom clusters in γ -brass structures with *I* and *R* cells

In the *R* cell site labels, + and - signs are used to distinguish *OH* and *CO* positions with components respectively along $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ relative to the centre of the cluster. *IT*1 and *OT*3 have components along $[111]$ whereas *IT*3 and *OT*1 have components along $[\bar{1}\bar{1}\bar{1}]$ from the centre of the cluster.

$I\bar{4}3m$ (No. 217)			$R3m$ (No. 160)		
Site label	Site set	Coordinate type	Site label	Site set	Coordinate type
<i>IT</i>	8(c)	$x_1x_1x_1$	<i>IT</i> 1	1(a)	$x_1x_1x_1$
<i>OT</i>	8(c)	$x_2x_2x_2$	<i>IT</i> 3	3(b)	$x_2x_2x_2$
<i>OH</i>	12(e)	$00z_3$	<i>OT</i> 1	1(a)	$x_3x_3x_3$
<i>CO</i>	24(g)	$x_4x_4z_4$	<i>OT</i> 3	3(b)	$x_4x_4z_4$
			<i>OH</i> 3+	3(b)	$x_5x_5z_5$
			<i>OH</i> 3-	3(b)	$x_6x_6z_6$
			<i>CO</i> 3+	3(b)	$x_7x_7z_7$
			<i>CO</i> 3-	3(b)	$x_8x_8z_8$
			<i>CO</i> 6	6(c)	$x_9y_9z_9$

Table 1. Crystal data for Cr_5Al_8 and V_5Al_8

Figures in parentheses represent standard errors in the last digits quoted.

	Cr_5Al_8 $R3m$ (No. 160)	V_5Al_8 $I\bar{4}3m$ (No. 217)
Space group		
Cell constants		
Primitive cell (~26 atoms)	$a' = 7.811$ (3) \AA $a' = 109.13$ (2) $^\circ$	Cell constant $a = 9.234$ (5) \AA
Body-centred cell (~52 atoms, pseudocubic)	$a = 9.057$ (6) \AA $\alpha = 89.28$ (5) $^\circ$	
Primitive cell volume	$V' = 371.4$ (8) \AA^3	Cell volume $V = 787.35$ \AA^3
Density		
D_m (pycnometric)	4.22 (3) g cm^{-3}	$D_m = 3.97$ (5) g cm^{-3}
D_x (for $\text{Cr}_{10}\text{Al}_{16}$)	4.26 (1)	$D_x = 3.968$
Number of formula units in primitive cell using D_m and Cr_5Al_8 composition	$Z = 1.98$ (2)	Formula units per cell $Z = 4$
Linear absorption coefficient (Mo $K\alpha$)	$\mu = 82.4$ cm^{-1}	$\mu = 69.2$ cm^{-1}

tion of the origin along the $[111]$ axis. $OT3$ in the $3(b)$ xxz -type site was selected to have $x = y = 0$, thereby fixing the origin.

Atomic scattering factors from the Thomas–Fermi–Dirac statistical model and corrections for anomalous scattering with $Mo\ K\alpha$ radiation were taken from *International Tables for X-ray Crystallography* (1968).

During the refinement, the $IT1$ site presented a problem in that agreement between $|F_c|$ and $|F_o|$ was best achieved by Al occupancy, but interatomic distances were inconsistent with this model and suggested occupancy by a smaller atomic species. This was resolved by placing Cr on $IT1$ and refining a fractional occupancy factor for this site which finally reached the value 0.497 ± 0.003 . For the final structure factor calculation, this fractional occupancy factor was set equal to 0.5. Other occupancy factors were taken as 1.0 and were not treated as variables in the least-squares refinements, since no similar occupancy problems were evident on these sites. The fractional occupancy of $IT1$ is consistent with and appears related to the fact that α is less than 90° (52-atom cell) as discussed below.

The final atomic parameters are given in Table 3 and this model was obtained by least-squares refinement of the 263 reflexions observable above the $3\sigma(I)$ threshold to give $R_1 = 0.049$ and a weighted $R_w = 0.039 \{ R_1 \equiv \sum | |F_o| - |F_c| | / \sum |F_o|; R_w \equiv [\sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} \}$. The weighting scheme used was $w = (0.07763 - 0.00296 |F_o| + 0.00003 |F_o|^2)^{-1}$. The coefficients were determined by grouping the observed reflexions into five ranges of $|F_o|$, each group with about 50 reflexions, and plotting the mean value of $| |F_o| - |F_c| |^2$ against the mean $|F_o|$ for each range. Then a function of the form $\sigma^2 = A + B |F_o| + C |F_o|^2$ was fitted by least squares to the plot and the weights chosen as $w = 1/\sigma^2$. Assigning a value zero to $|F_o|$ for the 144 'unobservable' reflexions, the weighted R_w

becomes 0.054 when all 407 reflexions are included. The final model showed no abnormalities in calculated electron-density and difference electron-density maps. The maximum heights of residual features in the difference maps were $+1.15$ and $-3.22 e \text{ \AA}^{-3}$ compared to peaks on the electron density map ranging from an average of $58.7 e \text{ \AA}^{-3}$ for sites containing only Al to $142 e \text{ \AA}^{-3}$ for sites containing only Cr. Electron density peaks at $IT1$ (0.5 Cr) and $OT3$ (Cr) were 57.3 and $100 e \text{ \AA}^{-3}$ respectively. The observed and calculated structure factors are given in Table 4.

A list of interatomic distances is given in Table 5, and the averaged distances between different atomic species are given in Table 6. In body-centred cubic γ -

Table 4. Observed and calculated structure factor amplitudes for Cr_5Al_8 and V_5Al_8

The reflexion indices for Cr_5Al_8 refer to the primitive rhombohedral cell, whereas those for V_5Al_8 refer to the body-centred cubic cell. For V_5Al_8 data, asterisks denote reflexions where $I_o < 2\sigma(I_o)$.

Cr_5Al_8				V_5Al_8				
hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
111	142	141	200	200	200			
200	108	108	111	142	141			
110	80	80	200	200	200			
100	57	57	111	142	141			
111	57	57	200	200	200			
010	42	42	111	142	141			
100	42	42	200	200	200			
111	42	42	111	142	141			
110	31	31	200	200	200			
100	31	31	111	142	141			
111	31	31	200	200	200			
010	21	21	111	142	141			
100	21	21	200	200	200			
111	21	21	111	142	141			
110	15	15	200	200	200			
100	15	15	111	142	141			
111	15	15	200	200	200			
010	10	10	111	142	141			
100	10	10	200	200	200			
111	10	10	111	142	141			
110	7	7	200	200	200			
100	7	7	111	142	141			
111	7	7	200	200	200			
010	5	5	111	142	141			
100	5	5	200	200	200			
111	5	5	111	142	141			
110	4	4	200	200	200			
100	4	4	111	142	141			
111	4	4	200	200	200			
010	3	3	111	142	141			
100	3	3	200	200	200			
111	3	3	111	142	141			
110	2	2	200	200	200			
100	2	2	111	142	141			
111	2	2	200	200	200			
010	1	1	111	142	141			
100	1	1	200	200	200			
111	1	1	111	142	141			
110	1	1	200	200	200			
100	1	1	111	142	141			
111	1	1	200	200	200			

Table 3. Structural parameters for γ - Cr_5Al_8 in the primitive rhombohedral $R3m$ cell

Site label	Occupancy	$R3m$ Site set	Fractional coordinates			Isotropic temperature factor B (\AA^2)
			x	y	z	
$IT1$	$\frac{1}{2}Cr^*$	$1(a)$ xxx	0.1795 (21) [†]			0.17 (7)
$IT3$	$\frac{1}{2}Cr + \frac{1}{2}Al$	$3(b)$ xxz	0.0055 (13)		-0.2096 (15)	0.55 (11)
$OT1$	Cr	$1(a)$ xxx	-0.3071 (11)			0.17 (4)
$OT3$	3Cr	$3(b)$ xxz	$0 \pm$		0.3451 (11)	0.46 (9)
$OH3+$	2Cr + Al	$3(b)$ xxz	0.3699 (3)		0.0306 (13)	0.25 (9)
$OH3-$	3Al	$3(b)$ xxz	-0.3608 (19)		-0.0095 (22)	1.28 (19)
$CO3+$	$\frac{1}{2}Cr + \frac{1}{2}Al$	$3(b)$ xxz	0.3608 (13)		0.5720 (15)	0.60 (11)
$CO3-$	3Al	$3(b)$ xxz	-0.2709 (15)		-0.6270 (19)	0.42 (13)
$CO6$	6Al	$6(c)$ xyz	-0.3179 (15)	0.2982 (10)	0.0533 (10)	0.84 (4)

* The $IT1$ site has a fractional occupancy of 0.5. See text for discussion of this.

[†] Figures in parentheses are the standard errors in the last digits quoted, as determined during the least-squares refinement.

[‡] The origin in space group $R3m$ was fixed by setting $OT3$ x equal to 0.

brasses the clusters of 26 atoms are roughly spherical in their overall shape. In rhombohedral Cr_5Al_8 where only one threefold symmetry axis along [111] exists, the ordering of atoms is such that smaller Cr atoms are predominant in the sites in that half of the cluster along the positive [111] direction. The larger Al atoms are predominant in the other half of the cluster. This feature shows up in the interatomic distances (Table 5) where distances between atoms within the positive [111] half of the cluster are shorter than those between atoms within the other half. Table 7 compares some of these distances with values for a typical cubic γ -brass cluster. Hence, the observed atomic ordering, together with an expected collapse of the positive [111] half of

the cluster whenever an *IT1* site is vacant, tends to give the clusters in Cr_5Al_8 a conical distortion compared to the roughly spherical clusters found in cubic γ -brasses,

Table 6. Average distances (\AA) between various atomic species

Atomic species	Average distance	Number of distances averaged
Cr-Cr	2.59	3
Cr-Mixed	2.62	30
Cr-Al	2.66	24
Mixed-Mixed	2.67	18
Mixed-Al	2.70	48
Al-Al	3.15	54

Table 5. Interatomic distances for the coordination polyhedra in Cr_5Al_8

A primed atom symbol denotes a neighbour in a different cluster. Estimated standard errors are typically $\pm 0.03 \text{ \AA}$.

Site	Neighbour	Number	Distance	Site	Neighbour	Number	Distance	
<i>IT1</i> ($\frac{1}{2}\text{Cr}$)	<i>IT3</i>	3	2.51 \AA	<i>OH3-</i> (Al)	<i>IT3</i>	2	2.66 \AA	
	<i>OT3</i>	3	2.59		<i>OT1</i>	1	2.63	
	<i>OH3+</i>	3	2.57		<i>OT3</i>	1	2.85	
	<i>CO3+</i>	3	2.53		<i>OH3+'</i>	1	2.63	
	<i>OT1</i>	1	3.87		<i>CO3-</i>	2	2.85	
<i>IT3</i> ($\frac{1}{2}\text{Cr} + \frac{1}{2}\text{Al}$)	<i>IT1</i>	1	2.51		<i>CO6</i>	2	3.17	
	<i>IT3</i>	2	2.74		<i>CO3+'</i>	1	2.78	
	<i>OT1</i>	1	2.48		<i>CO3-'</i>	1	2.62	
	<i>OT3</i>	2	2.64		<i>CO6'</i>	2	2.96	
	<i>OH3+</i>	1	2.72		<i>CO6'</i>	2	3.80	
	<i>OH3-</i>	2	2.66		<i>CO3+</i> ($\frac{1}{2}\text{Cr} + \frac{1}{2}\text{Al}$)	<i>IT1</i>	1	2.53
	<i>CO3-</i>	1	2.77			<i>OT3</i>	1	2.70
	<i>CO6</i>	2	2.64	<i>OT1'</i>		1	2.60	
	<i>OT3'</i>	1	3.45	<i>OH3+</i>		2	2.58	
<i>OT1</i> (Cr)	<i>IT3</i>	3	2.48	<i>OH3-'</i>		1	2.78	
	<i>OH3-</i>	3	2.63	<i>OH3+'</i>		1	3.54	
	<i>CO3-</i>	3	2.70	<i>CO3+</i>		2	2.69	
	<i>CO3+'</i>	3	2.60	<i>CO3-'</i>		2	2.69	
	<i>IT1</i>	1	3.87	<i>CO6'</i>		2	2.76	
<i>OT3</i> (Cr)	<i>IT1</i>	1	2.59	<i>CO3-</i> (Al)		<i>IT3</i>	1	2.77
	<i>IT3</i>	2	2.64		<i>OT1</i>	1	2.70	
	<i>OH3+</i>	2	2.76		<i>OT3'</i>	1	2.58	
	<i>OH3-</i>	1	2.85		<i>OH3-</i>	2	2.85	
	<i>CO3+</i>	1	2.70		<i>OH3-'</i>	1	2.62	
	<i>CO6</i>	2	2.58		<i>OH3+'</i>	1	2.81	
	<i>CO3-'</i>	1	2.58		<i>CO6</i>	2	3.69	
	<i>CO6'</i>	2	2.68		<i>CO3+'</i>	2	2.69	
	<i>IT3'</i>	1	3.45		<i>CO6'</i>	2	2.89	
	<i>OH3+</i> ($\frac{2}{3}\text{Cr} + \frac{1}{3}\text{Al}$)	<i>IT1</i>	1		2.57	<i>CO6'</i>	2	3.28
		<i>IT3</i>	1		2.72	<i>CO6</i> (Al)	<i>IT3</i>	1
<i>OT3</i>		2	2.76	<i>OT3</i>	1		2.58	
<i>OH3-'</i>		1	2.63	<i>OT3'</i>	1		2.68	
<i>CO3+</i>		2	2.58	<i>OH3+</i>	1		2.74	
<i>CO6</i>		2	2.74	<i>OH3-</i>	1		3.17	
<i>CO3-'</i>		1	2.81	<i>OH3+'</i>	1		2.64	
<i>CO3+'</i>		1	3.54	<i>OH3-'</i>	1		2.96	
<i>CO6'</i>		2	2.64	<i>OH3-'</i>	1		3.80	
				<i>CO6</i>	1		3.12	
			<i>CO3-</i>	1	3.69			
			<i>CO6'</i>	2	2.82			
			<i>CO3+'</i>	1	2.76			
			<i>CO3-'</i>	1	2.89			
			<i>CO3-'</i>	1	3.28			

Table 7. *Some interatomic distances (Å) in γ -Cr₅Al₈ and in γ -Cu₅Zn₈ which show the cluster distortion*

Sites in γ -Cr ₅ Al ₈	Distance	Sites in γ -Cu ₅ Zn ₈	Distance
IT1—IT3	2.51	IT—IT	2.74
IT3—IT3	2.74		
OH3+—CO3+	2.58	OH—CO	2.82
OH3+—CO6	2.74		
CO6—CO6	3.12	CO—CO	3.47
CO6—CO3	3.69		
CO3+—CO3+	2.69	CO—CO	3.47

with the point of the cone directed along the positive [111] direction. As clusters with this conical distortion are packed together, the rhombohedral angle with α less than 90° (52-atom cell) results. Similar ordering and/or vacancies might be anticipated in other rhombohedral γ -brasses with $\alpha < 90^\circ$.

In cubic γ -phases, IT and OT sites are 12-coordinated, the OH sites are 13-coordinated, and CO sites can be regarded as 11, 13 or 15-coordinated, depending on the particular phase considered. However, in Cr₅Al₈, the OH3-, CO3- and CO6 sites are all 15-coordinated, whereas all others have CN 12. This again emphasizes the conical nature of the clusters in that the OH3+ sites have gone from 13 to 12-coordination, whereas the OH3- have gone to 15-coordination.

The present results are very similar to the structure of γ -Cr₅Al₈ determined by Bradley & Lu (1937b). There are minor differences in the species of atoms which occupy several of the sites (e.g. IT3, OH3+ and CO3+). However, the overall preponderance of smaller atomic species in the positive [111] end of the cluster and of larger atoms in the negative [111] end is easily evident in the model of Bradley & Lu. Most of the differences in atomic coordinates are also minor. The only major discrepancies with the present single-crystal work are in the occupation and coordinates of the IT1 and OT1 sites. In Bradley & Lu's model, the IT1 site is fully occupied by Cr and the OT1 site by Al, with the result that these sites are further from the centre of the cluster than in the present work. It is evident that Bradley & Lu were able to determine the structure of γ_2 -Cr₅Al₈ quite accurately with only powder X-ray diffraction data available for their analysis. Finally, it is suggested from the agreement of the two studies, either that our crystals quenched from 1215°C transformed to the γ_2 phase on quenching, or that the structures of the γ_1 and γ_2 phases are very similar, with the main differences occurring in the occupancies of the IT1 and OT1 sites.

Structure of V₅Al₈

δ -(Al-V) forms peritectically at 1670°C and has a very narrow range of composition at low temperatures

(Hansen, 1958). An alloy containing 39.2 at.% V was prepared from 99.9%-pure V and 99.99%-pure Al (A. D. Mackay Co.) by arc melting under an argon atmosphere several times to ensure homogeneity. The weight loss on melting was very small. The metal pellet was then annealed at 1220°C under vacuum (3×10^{-6} torr) in a sealed quartz tube for 330 h. Subsequently the alloy was quenched, resulting in its fragmentation. Suitably sized fragments were then re-annealed under similar conditions at 800°C for a few hours.

Preliminary rotation, Weissenberg and precession X-ray diffraction photographs were used to select a good single crystal for intensity measurements. A cubic body-centred lattice was confirmed from the systematic absences, agreeing with the work of Carlson *et al.* (1955).

The cell constant was refined by a least-squares fit of 2θ values measured for eight reflexions on the General Electric XRD-6 X-ray diffractometer, equipped with a scintillation counter and pulse-height analyser. Zr-filtered Mo K α radiation was used ($\lambda = 0.7107$ Å). Crystal data are given in Table 1.

Intensity data were collected by a θ - 2θ scan method with a scan range in 2θ of $\pm(0.9 + 0.3 \tan \theta)^\circ$. The background was recorded at the beginning and end of each scan. One thousand nine hundred and forty-one reflexions with $2\theta < 70^\circ$ (Mo K α) in two quadrants were measured with the ϕ axis of the goniostat parallel to the [110] direction in the crystal. Six strong reflexions were repeatedly checked after every 100 measurements in order to apply a small correction (<5%) for the fluctuation of intensities during the course of this data collection.

Equivalent reflexions for space group $I\bar{4}3m$ were averaged and of these 140 had intensities larger than the background by $2\sigma(I)$ and were considered to be observable. Sixty-four unobservable reflexions were given zero weight in least-squares refinement and the calculated structure factors for them were within the $2\sigma(I)$ limit. The crystal was approximately cylindrical with a mean diameter of 0.06 mm. Since μR (Mo K α) was only 0.2, no absorption corrections were made. Atomic scattering curves from the Thomas-Fermi-Dirac statistical model were used (*International Tables for X-ray Crystallography*, 1968) and corrections for anomalous dispersion were included in the final analysis. Full-matrix least-squares refinements were begun starting with the 'ideal' γ -brass coordinates suggested by von Heidenstam, Johansson & Westman (1968). The function minimized was $\Sigma(|F_o| - |F_c|)^2$, where each observed reflexion was given unit weight. The final R_1 value (observed reflexions only) was 0.049. A separate refinement was carried out including unobserved reflexions and with an empirical weighting function $w = [100.0 - |F_o| + 0.003|F_o|^2]^{-1}$ where relative coefficients in the weighting function were determined by a method for fitting a parabolic function

Table 8. γ -V₅Al₈ coordinates and isotropic thermal parameters

Site label	Occupancy	$I\bar{4}3m$ Site set	Fractional coordinates		B (Å ²)
			x	z	
<i>IT</i>	4Al + 4V	8(c) <i>xxx</i>	0.1062 (3)*		0.52 (6)
<i>OT</i>	8V	8(c) <i>xxx</i>	0.8300 (3)		0.30 (6)
<i>OH</i>	4Al + 8V	12(e) <i>00z</i>		0.3522 (42)	0.53 (5)
<i>CO</i>	24Al	24(g) <i>xxz</i>	0.3087 (3)	0.0394 (5)	0.63 (6)

* Figures in parentheses are the standard errors in the last digits quoted, as determined during the least-squares refinement.

Table 9. Interatomic distances (Å) and coordinations for γ -V₅Al₈

Standard deviations for distances are ≈ 0.02 Å. A prime on a site label denotes an atom in a neighbouring cluster.

Site	Neighbours	Number	Distance	Site	Neighbours	Number	Distance
<i>IT</i> ($\frac{1}{2}$ Al + $\frac{1}{2}$ V)	<i>IT</i>	3	2.77	<i>OH</i> ($\frac{1}{2}$ Al + $\frac{1}{2}$ V)	<i>IT</i>	2	2.66
	<i>OT</i>	3	2.68		<i>OT</i>	2	2.79
	<i>OH</i>	3	2.66		<i>OH'</i>	1	2.73
	<i>CO</i>	3	2.72		<i>CO</i>	4	2.90
<i>OT</i> (V)	<i>IT</i>	3	2.68	<i>CO</i> (Al)	<i>IT</i>	1	2.72
					<i>OT</i>	1	2.65
					<i>OT'</i>	1	2.70
					<i>OH</i>	2	2.90
	<i>OH</i>	3	2.79		<i>OH'</i>	1	2.69
					<i>OH'</i>	1	3.04
					<i>CO</i>	2	3.52
					<i>CO'</i>	4	2.77
<i>CO</i>	3	2.65	<i>CO'</i>	2	3.61		
			<i>CO'</i>	4	2.77		
			<i>CO'</i>	2	3.61		
			<i>CO'</i>	2	3.61		

similar to that described above for Cr₅Al₈. This refinement gave $R_w = 0.071$ and atomic coordinates that were indistinguishable from those previously found. The lowest R_1 value was obtained for the ideal composition, V₅Al₈, which is consistent with the measured density (Table 1). The positional parameters and temperature factors are given in Table 8 and the interatomic distances, which appear normal for a γ -brass, are listed in Table 9. Structure factors have been included in Table 4.

Discussion

Because of the transition metals occurring in the γ -brasses with rhombohedral cells, the valence-electron concentration is hard to assess. The Al–Cu phase is the only one without a transition-metal atom, but the rhombohedral structure may contain vacant sites.* If

* Neither Bradley, Goldschmidt & Lipson (1938), Hume-Rothery, Betterton & Reynolds (1951–52), nor Westman (1965) explicitly measured densities of γ -Al–Cu alloys and earlier estimates of atomic defects not based on knowledge of the rhombohedral cell are unsound. Nevertheless Westman (1965) clearly shows a decrease of a with increasing Al content in the rhombohedral phase indicating a defect structure where Cu atoms are omitted. Rough estimates based on these data suggest that the electron concentration in rhombohedral γ -Al–Cu might be as low as 88 electrons per 52-atom cell, and it could be as high as 92.5 or 93.

all sites are fully occupied the Al–Cu phase would be homogeneous over the range from about 92.5 to 94.7 electrons per 52-atom cell. If in the Al–Cr and Al–Mn phases the transition metal contributes no electrons to the conduction band, they would contain approximately 93.6 to 97.5 and 93.6 outer electrons per 52-atom cell respectively. Under similar conditions Ga–Cr, Ga–Mn and Ga–Fe phases would have about 78, 72 and 72 outer electrons per 52-atom cell, or about 100 if the transition metal contributed something like one electron to the conduction bands.

Such evidence suggests that these γ -brasses with R cells probably occur at electron concentrations higher (say about 95 electrons per 52-atom cell) than those at which cubic γ -brasses are obtained. On this basis, it is possible to develop a hypothesis that the R phases are the result of a distortion which is stabilized by band-structure energy.

It is quite impossible to discuss details of Fermi surfaces and Brillouin zones for γ -brass structures with 26 or 52 atoms per primitive cell; however, we can illustrate the principles of the hypothesis in terms of the reduced zone for γ -brass with the I cell, assuming an electron concentration of about 1.7 electrons per atom. The reduced zone is a rhombic dodecahedron made up of reciprocal-lattice planes corresponding to $\{110\}$ real-space planes. Let us assume that these planes are

touched by the Fermi surface and that no overlap occurs so that the density of states, $N(E)$, is a decreasing function with increasing electron concentration.

Thus the electrons have to be accommodated at higher and higher energies as the electron concentration increases by alloying so that eventually some other phase, X , becomes more stable. Diagrammatic free-energy curves representing this situation at a given temperature are shown in Fig. 1(a) where the γ -phase boundary occurs at about 88 electrons per 52-atom cell.

Suppose, however, there is a rhombohedral distortion of the structure with $\alpha < 90^\circ$, so that the six reciprocal planes (110), (101), (011), ($\bar{1}\bar{1}0$), ($\bar{1}0\bar{1}$) and ($0\bar{1}\bar{1}$) move in towards the origin and the other six planes ($\bar{1}\bar{1}0$) \bar{C} move away from the origin. Overlap of the Fermi surface on the six planes that moved towards

the origin would exert forces on the planes in the direction of the origin (Jones, 1934) and thus stabilize the distortion. Such overlap will increase $N(E)$ so that the electrons are accommodated at a significantly lower energy than in the cubic structure. A possible variation as a function of the angle of distortion, α , of the free energy of the rhombohedral structure with zone overlap, say at an electron concentration of 95 electrons per 52-atom cell, is shown in Fig. 1(b). Beyond a certain degree of distortion the rhombohedral phase has a lower free energy than the other phase, X , and hence becomes the stable phase. Fig. 1(c) shows hypothetical free-energy curves at a given temperature for cubic γ -brass, for the X phase and for rhombohedral γ -brass with, say, $\alpha = 88.5^\circ$, all shown as a function of electron concentration. It indicates how the R phase rather than X becomes stable at higher electron concentrations, and furthermore that a homogeneous transformation between the cubic and rhombohedral γ -brass phases is impossible; indeed in the Al-Cu system a two-phase region separates the γ -brass phases with cubic and rhombohedral structures.

The principles that have been discussed here in terms of the reduced zone for the I -cell γ -brass, should apply equally well for the 24th or whatever Brillouin zone is appropriate for the I -cell γ -brass and thus it is shown that the rhombohedral structure can be accounted for as a band-structure-energy-stabilized distortion of the cubic structure, which is stable at higher electron concentrations than those permitted for the cubic structure.

It is surprising to find that V_5Al_8 has the I cell whereas Cr_5Al_8 has the R cell, since there are essentially no vacant sites in V_5Al_8 and it would be expected to have the same high electron concentration as Cr_5Al_8 (i.e. about 96 per 52-atom cell, assuming the transition metal contributes no electrons to the conduction band). If the above hypothesis for the stability of phases with the R cell is correct, since V_5Al_8 has a cubic γ -brass structure, it must be presumed that V absorbs some electrons (provided by Al) into its hybridized bands which have mainly d character. If one electron per V atom were absorbed, this would allow three filled bands below the Fermi level and the electron concentration in partly filled conduction bands would be 76 per 52-atom cell for the composition V_5Al_8 ; however, it is unknown whether the absorption of electrons would be as great as this. Indeed, there is now some indirect evidence that such behaviour might be expected. Coppens (1975) has reported that electron density determinations of V_3Si with the β -W structure indicate that the V atoms absorb some 0.5 to 1.0 electrons from Si. Such behaviour would not, however, be expected for Cr in Cr_5Al_8 , since it already has six electrons provided that it contributes no net electrons to the partly filled conduction bands; neither is it to be expected for the other phases with R cells formed by Mn and Fe, since Fe and Mn have more than six outer electrons and are, therefore, more

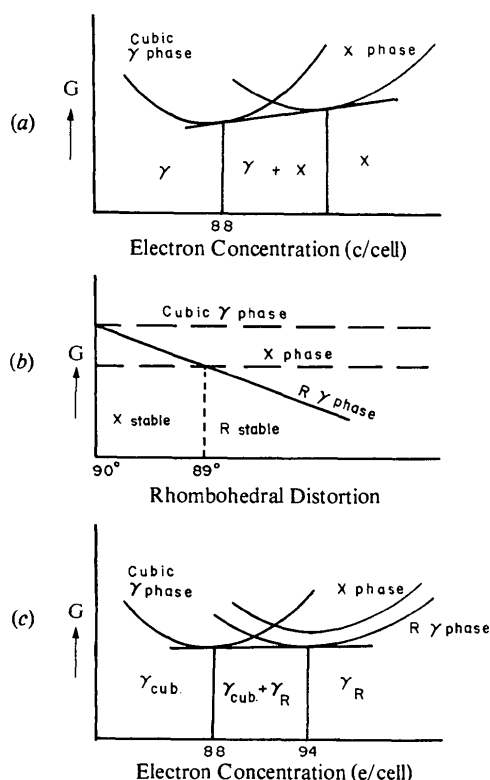


Fig. 1. (a) Hypothetical free-energy curves at a given temperature and as a function of electron concentration for a cubic γ -brass phase and another phase, X , indicating regions of stability of γ , ($\gamma + X$) and X . (b) Hypothetical variation of the free energy of a rhombohedral γ -brass phase as a function of distortion angle, α , ($< 90^\circ$) at a given temperature and electron concentration (say 95 electrons per 52-atom cell). Also indicated are the free energies of the cubic γ -brass and X phase at the same temperature and electron concentration. (c) Hypothetical free-energy curves at a given temperature and as a function of electron concentration for a cubic γ -brass phase, a rhombohedral γ -brass phase (with, say, $\alpha = 88.5^\circ$) and the X phase. Regions of stability of cubic γ , (cubic $\gamma +$ rhombohedral γ) and rhombohedral γ are indicated.

likely to contribute electrons to the conduction bands than absorb them.

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The Crystal and Molecular Structure of (\pm)-Azabiotin Hydrochloride Monohydrate, the Nitrogen Analog of Biotin

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The structure and stereochemistry of (\pm)-azabiotin hydrochloride has been accurately established by three-dimensional X-ray diffraction techniques. The crystals are triclinic, $P\bar{1}$, with crystal data $a = 7.628$ (2), $b = 13.145$ (3), $c = 7.185$ (1) Å, $\alpha = 99.70$ (1), $\beta = 106.37$ (2), $\gamma = 90.27$ (2)°, $Z = 2$ formula units of $\text{C}_{10}\text{H}_{20}\text{ClN}_2\text{O}_4$. The structure was solved by direct methods and refined to a conventional discrepancy index $R = 0.039$ for 1455 diffractometer data for which $I \geq 3\sigma(I)$. The crystals comprise a racemic mixture of the azabiotin cation protonated at N(1), with one chloride anion and one water of solvation per cation. The three asymmetric centers have the same relative stereochemistry found in biotin. The relevant bond distances and angles are similar to those found in biotin and dethiobiotin. This includes an elongated carbonyl distance [1.243 (4) Å] and shortened C–N distances [1.344 (4) and 1.349 (4) Å] in the ureido moiety. The bicyclic ring system is highly asymmetric in contrast to those found in biotin and dethiobiotin. The valeryl side chain is fully extended and essentially strain-free. A complex three-dimensional hydrogen-bonding network binds the entire crystal together.

Introduction

Biotin (I), a member of the B complex of vitamins, serves as a coenzyme for several important carboxylases including propionyl CoA carboxylase, β -methylcrotonyl CoA carboxylase, acetyl CoA carboxylase,

and oxalosuccinate-acetyl CoA transcarboxylate (Langer & Gyorgy, 1968). The vitamin is covalently linked to the enzyme *via* an amide bond involving the carboxyl group of biotin and the ϵ -amino group of a lysine residue. There is much evidence to suggest that, prior to transfer to the substrate, carbon dioxide