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Copper-Gallium,  $\gamma_1\text{Cu}_9\text{Ga}_4$ 

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**Abstract.**  $\gamma_1\text{Cu}_9\text{Ga}_4$  is one of the three  $\gamma$ -brass-like phases with approximate formula  $\text{Cu}_9\text{Ga}_4$ . Cubic,  $P\bar{4}3m$ ;  $a=8.747$  (2) Å;  $Z=4$ ;  $D_m=8.471$ ;  $D_x=8.441$  g cm $^{-3}$ ;  $\mu(\text{Mo } K\alpha)=455$ . The structure was refined from single-crystal diffractometer data to a weighted  $R$  value of 0.054 for 140 observed reflexions. The alloy has a typical  $\gamma$ -brass structure with a primitive lattice. Ga-Ga distances of 3.08 Å are in agreement with the atomic size of Ga discussed in terms of pseudo-potential theory.

**Introduction.** Using powder X-ray diffraction methods, Betterton & Hume-Rothery (1951-52) characterized three slightly different  $\gamma$  phases in the Cu-Ga system in the composition range from 30 to 42.5 at.% Ga. We now report a single-crystal study of the structure of the phase called  $\gamma_1\text{-Cu}_9\text{Ga}_4$ .

An alloy was prepared from 99.999% Cu and Ga (A. D. MacKay Inc.) by repeated melting *in vacuo*. The ingot was annealed to render it homogeneous and then shattered into small fragments which were finally annealed in a Pyrex tube for 11 days at 551°C and slowly cooled to room temperature. A suitable single crystal was selected and examined by rotation, Weissenberg and precession photographs. The cell constants were refined by the least-squares method from the  $2\theta$  (Zr-filtered Mo  $K\alpha$ ,  $\lambda=0.7107$  Å) values measured for six reflexions on the General Electric diffractometer, which is equipped with a scintillation counter and pulse height analyser. This same instrument was used for measuring the intensities employing a  $\theta$ - $2\theta$  scan method with a scan range in  $2\theta$  of  $\pm(0.9+0.3 \tan \theta)$  degrees. The background was measured at the beginning and end of each scan. The small but approximately cylindrical crystal with mean diameter of 0.06 mm was mounted with [011] along the  $\phi$  axis of the goniostat. Since  $\mu R=1.4$ , no absorption corrections were made.

A total of 1214 reflections with  $2\theta < 70^\circ$  (Mo  $K\alpha$ ) of the first quadrant were measured. Among these were four strong standard reflexions which were repeatedly measured after each 100 reflexions, the fluctuations being less than 5%. The equivalent reflexions were then averaged giving 243 independent reflexions, of which 140 had intensities greater than the background by  $1.5\sigma_I$  and were considered observed. The unobserved reflexions were given zero weight in the final analysis.

Full-matrix least-squares refinements were carried out starting with coordinates of  $\text{Cu}_9\text{Al}_4$  (Westman, 1965; Heidenstam, Johansson & Westman, 1968) which was believed to be isostructural with  $\text{Cu}_9\text{Ga}_4$ . Atomic scattering curves from the Thomas-Fermi-Dirac statistical model (*International Tables for X-ray Crystallography*, 1962) were used. Among numerous models tried, the reported distribution of atoms gave the lowest  $R$  and gave interatomic distances which were consistent with the sizes of the atomic species. The function minimized is  $\sum w(|F_o| - |F_c|)^2$  where  $w = (150 - F_o + 0.0033F_o^2)^{-1}$  and the final weighted  $R$  is 0.054. The positional and temperature parameters are given in Table 1.\*

**Discussion.** The structure can be described in terms of clusters  $A$  and  $B$ , each composed of four crystallographic sites: IT (inner tetrahedron), OT (outer tetrahedron), OH (octahedron) and CO (cubo-octahedron) (Bradley & Jones, 1933). It is thus an ordered form of the archetype  $\gamma$ -brass structure,  $\text{Cu}_5\text{Zn}_8$ , which has an  $I$  lattice. The ordering on IT sites appears to result

\* The interatomic distances and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30636 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional and thermal parameters for  $\gamma_1\text{Cu}_9\text{Ga}_4$ 

Cluster site*	Atom	Point set	$x$	$z$	$B$ (Å $^2$ )
$A$ IT	4Ga	4( $e$ ) $xxx$	0.1244 (7)†		0.8 (2)
$A$ OT	4Cu	4( $e$ ) $xxx$	-0.1685 (12)		1.2 (2)
$A$ OH	6Cu	6( $f$ ) $00z$		0.3534 (13)	1.0 (2)
$A$ CO	3Ga+9Cu	12( $i$ ) $xxz$	0.3167 (7)	0.0279 (12)	1.2 (1)
$B$ IT	4Cu	4( $e$ ) $xxx$	0.6034 (8)		1.2 (2)
$B$ OT	4Cu	4( $e$ ) $xxx$	0.3232 (9)		0.8 (2)
$B$ OH	6Cu	6( $f$ ) $00z$		0.8564 (13)	1.0 (2)
$B$ CO	9Ga+3Cu	12( $i$ ) $xxz$	0.8115 (7)	0.5352 (11)	1.2 (1)

\* See Discussion for this notation.

† The standard deviations in parentheses refer to the last digits quoted.

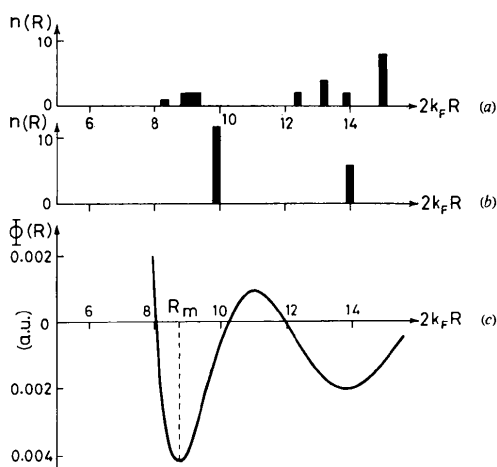


Fig. 1. Number of neighbours  $n(R)$  at distances  $R$ , (a) in the Ga structure, and (b) in Ga with hypothetical f.c.c. structure, together with (c) the interaction potential  $\Phi(R)$  for Ga. After Heine & Weaire (1970).

from the inability to mix components of different size (say greater than 8%) randomly in the inner tetrahedral sites. The same effect may cause the superstructure reported for  $\text{Fe}_3\text{Zn}_{10}$  (Brandon, Brizard, Chieh, McMillan & Pearson, 1974).

The one remarkable feature of the structure is the Ga-Ga distance of 3.08 Å found in the cluster  $A$  inner tetrahedron of Ga atoms which have overall coordination number 12. As we shall briefly show, the pseudo-potential theory explanation for elemental Ga having an orthorhombic rather than a face-centred cubic (f.c.c.) structure (Heine, 1968) has a direct consequence that the CN12 diameter of Ga is 3.03 Å, instead of the generally accepted empirical diameter of 2.82 Å, which is obtained by averaging the seven closest distances in stable orthorhombic Ga and then using Pauling's bond order equation to convert the diameter to CN12 (*cf.* Teatum, Gschneidner & Waber, 1960). Thus, the pseudo-potential result, which has not previously been pointed out, gives a Ga CN12 diameter (3.03 Å) in good agreement with that observed in  $\gamma_1\text{-Cu}_9\text{Ga}_4$  (3.08 Å).

Pseudo-potential theory shows that Ga in an f.c.c. structure would have its closest vectors on the rising part of the rearrangement potential curve,  $\Phi(R)$ , indicating structural instability (Heine & Weaire, 1970). A more stable structure could be obtained by shortening some vectors so that they move towards the first

minimum in  $\Phi(R)$  and lengthening others so that they move towards the second minimum (Fig. 1). The CN12 diameter of Ga should, according to the theory, be given by the interatomic distance in a hypothetical f.c.c. Ga structure which has the same atomic volume as orthorhombic Ga, namely 19.595 Å<sup>3</sup>. The diameter of a Ga atom in f.c.c. arrangement which gives this atomic volume is 3.027 Å.

Appeal to empirical data to support one or other point of view of the CN12 diameter of Ga is of little help; for example, the apparent atomic diameter of Ga obtained from solid solutions of Ga in Cu, Ag and Au, and obtained from many intermetallic phases containing Ga appears to be close to 2.82 Å, whereas in the Ga-rich compounds  $\text{PdGa}_5$ ,  $\text{FeGa}_3$  and  $\text{CoGa}_3$  (where the contraction in atomic volume compared to the elements is less than 10%) and in  $\gamma_1\text{-Cu}_9\text{Ga}_4$ , the average values of all Ga-Ga distances in the unit cells for neighbours in convex coordination polyhedra as defined by Frank & Kasper (1958) with average coordination about 12 are indeed close to 3.03 Å, although some 40 to 50% of the actual Ga-Ga distances may lie within  $\pm 0.05$  Å of 2.82 Å! Thus the crystal structure and atomic diameter of Ga remain a pleasant enigma which quantitative theoretical study must solve.

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