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Crystal Perfection in a Non-Centrosymmetric Alloy. Refinement and Test of Twinning of the γ -Cu₃Al₄ Structure

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The crystal structure of Cu₃Al₄ has been refined on the basis of 114 independent structure factors, averaged from a set of 2416 intensity measurements with a diffractometer on a spherical crystal of 0.05 mm diameter. Graphite-monochromatized Cu K α radiation was used. The final *R* value was 2.4% when corrections for absorption and extinction had been applied. Anisotropic thermal parameters were introduced and shown to be significant. The occurrence of coherently scattering antiphase domains was found to be less than 1%. All equivalent reflections and Friedel pairs were recorded with graphite-monochromatized Mo K α radiation for ten selected index combinations. Observed and calculated anomalous dispersion effects were found to match closely, indicating that incoherent twinning was also practically non-existent.

Introduction

In a previous investigation of the Cu–Al system, a phase of distorted γ -brass type was found to have rhombohedral symmetry (Westman, 1965). Later, an attempt was made to solve its structure, but a mono-crystal could not be prepared (Lindahl & Westman, 1967). Neither could single crystals be obtained of the γ -Cu₇Hg₈ phase; its structure had to be inferred from X-ray powder diffraction data (Lindahl & Westman, 1969). Crystals of these phases always appeared to occur as twins; and because of the very small deviation of the rhombohedral angle from 90°, the reflections from different crystal individuals could not be clearly resolved.

Thus the question arose whether twinning would always preclude single-crystal analysis of γ -brass structures with R cells. Recently, however, Brandon, Pearson, Riley, Chieh & Stokhuyzen (1977) have been able to prepare single crystals of rhombohedral Cr₅Al₈, and they do not mention difficulties due to twinning.

The ubiquitous twinning in the rhombohedral phases also suggested that an analogous phenomenon might cause some of the difficulties encountered in refining the structures of cubic γ -brasses: standard deviations of refined parameters tend to be rather large, and reliability indices, R , range from 5 to 15% in spite of correction of X-ray data for absorption and even extinction.

Also, electron-microscopic observations on Cu₉Al₄ have revealed domains in the crystals (Gabriel Torres & Radcliffe, 1975), which might be construed as anti-phase domains or, possibly, twin individuals of other descriptions. The authors themselves attribute different compositions to different domains; judging from their data, however, their description does not seem to fit the stoichiometry. Antiphase domains have, moreover, been observed in Cu₅Zn₈ (Morton, 1975).

We therefore resolved to test a cubic γ -brass crystal for signs of twinning or similar defect structure, and selected Cu₉Al₄ as being fairly easy to prepare, having rather low X-ray absorption, but being nevertheless quite unsatisfactorily refined, with an R value of 14.5% (Heidenstam, Johansson & Westman, 1968). As mentioned above, distinguishable domains have been observed in that very phase; we also convinced ourselves that the anomalous X-ray dispersion phenomenon could be used as one test of the nature of possibly occurring domain structure.

Experimental

Spherical single crystals of Cu₉Al₄ could be prepared by partial remelting of small alloy fragments in a plasma furnace according to a procedure described in detail in a separate article (Arnberg & Westman, 1978).

A Guinier photograph of the starting material yielded a lattice-parameter value $a = 8.7068$ (3) Å, and hence the mole fraction of Al $x_{\text{Al}} = 0.320$ (Westman, 1965). This analysis corresponds to a unit-cell content of Cu_{35.4}Al_{16.6}. The same composition was subsequently found for the spherical single crystal selected for X-ray work (see below).

We mounted the crystal, which had a diameter of 0.05 ± 0.01 mm, on a PW 1100 automatic X-ray diffractometer and recorded 2416 reflections, for $|h|$, $|k|$, $|l| < 9$ and $\theta < 67^\circ$, with graphite-crystal-monochromatized Cu $K\alpha$ radiation. The peaks were continuously scanned, $\Delta\theta = 1.20^\circ$ with a speed of $0.02^\circ \text{ s}^{-1}$, and the background measured at each end of the scans. A refinement of the crystallographic unit-cell parameter from these data yielded $a = 8.707$ (1) Å, *i.e.* the same value as before the plasma melting. Averaging of the intensities resulted in 150 independent I_o values, which were then corrected for absorption, assuming the crystal to be an ideal sphere with $\mu r = 0.90$. The absorption factors calculated ranged between 2.8 and 3.6.

In order to test the perfection of the crystal by means of the anomalous dispersion effect we also collected intensity data with monochromatized Mo $K\alpha$ radiation, which, however, is absorbed more than Cu $K\alpha$ in this crystal: $\mu r = 1.5$ and absorption factors in the range 6.4–7.4 for the recorded data. Ten independent reflections were chosen as having reasonable combinations of intensity and expected relative difference between Friedel pairs. For each of the ten index combinations we measured all reflections and their Friedel pairs over the whole reciprocal sphere, *i.e.* 48 measurements for the general hkl reflection. The scanning conditions were the same as for Cu radiation.

In the structure refinements we used scattering factors from Cromer & Waber (1965) and dispersion corrections given by Cromer & Liberman (1970). Least-squares refinements and structure factor calculations were carried out with the program *UPALS* on an IBM 360/75 computer.

Structure refinement

In order to use diffraction data to test for crystal imperfection we must first refine the ideal structure model as far as possible. Starting with the parameters given by Heidenstam, Johansson & Westman (1968), we used all the 150 independent structure factor amplitudes derived from the absorption and L_p -corrected Cu $K\alpha$ material in a refinement with unit weights, which yielded $R = 100 (\sum ||F_o| - |F_c|| / \sum |F_o|) = 8.5\%$. Changing to a σ^{-2} weighting scheme reduced R to 7.0%. The isotropic thermal parameters were all positive, in the interval 0.2–0.7 Å².

Removal of weak reflection intensities, with $\sigma(I)/I > 0.16$, which in several cases included contributions

from single measurements with $I_{\text{peak}} - I_{\text{back}} < 0$, and also of the strong 330 reflection which appeared to be appreciably affected by extinction, left us with 114 'reliable' structure amplitudes. A continued refinement on the basis of this material proceeded to $R = 4.5\%$; this value was further reduced to $R = 3.9\%$ when another four strong reflections were excluded from the treatment.

Presumably, then, a correction for extinction would be warranted. When it had been carried out, with the strong reflections again included in the data set, the structure model refined to $R = 3.1\%$, with isotropic thermal parameters ranging from 0.6 to 1.3 Å². The extinction factors lay in the range 1.00–1.40. At this stage an appropriate weighting scheme had been found to be $w = [1.00\sigma^2 + (0.005|F_o|)^2]^{-1}$, with σ derived from counting statistics.

Finally, we also refined a structure model including anisotropic thermal parameters, with the same weighting scheme as above. As a result the reliability-index value dropped from $R = 3.11$ to $R = 2.44\%$. That this improvement, upon introduction of 14 further

parameters to describe anisotropic thermal motion, is significant with better than 99.5% probability can be shown by the test introduced by Hamilton (1965): $\mathcal{R}_0 = 3.11/2.44 = 1.27$ is larger than the theoretically calculated (or, rather, interpolated in Hamilton's tables) $\mathcal{R}_{14, 114, 0.005} = 1.14$, for 14 additional parameters, 114 independent observational data and a probability of 0.005 for the change of model not to be significant.

Table 1 gives the refined structural parameters of Cu₉Al₄, in space group $P43m$ (No. 215).* Fig. 1 shows stereopair pictures of the atoms in clusters *A* and *B* (cf. description in Heidenstam, Johansson & Westman, 1968). In Fig. 2 is shown a map of one of the 'most useful planes' ($\bar{1}\bar{1}0$) in the cell, according to Samson (1964), containing the thermal ellipsoids of all types of atoms in the structure.

* A list of structure factors and a table of interatomic distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33238 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

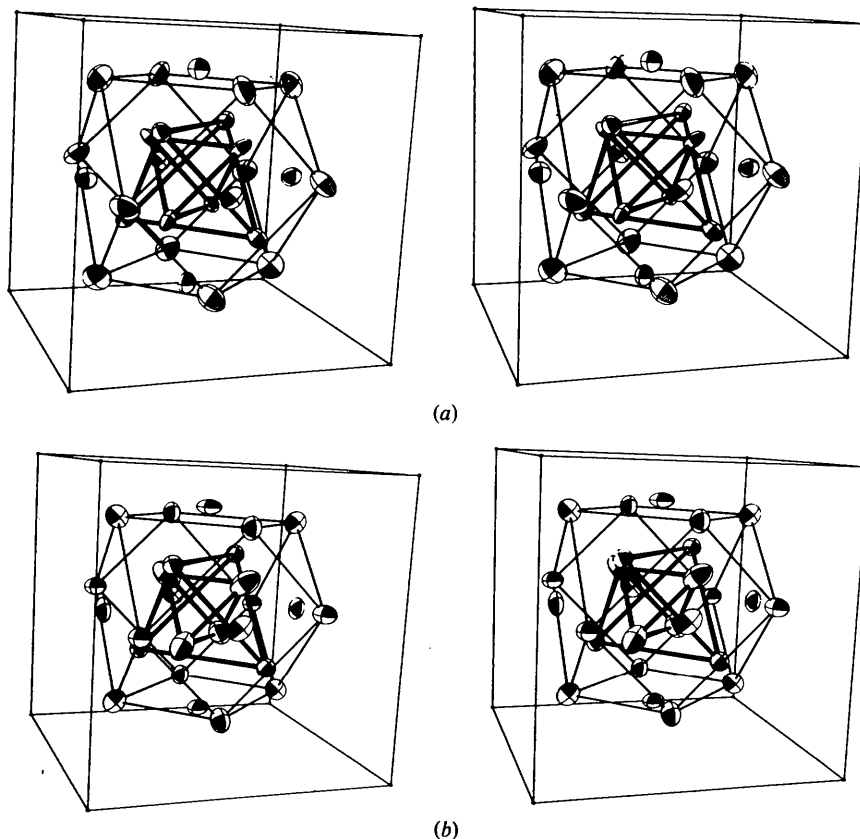


Fig. 1. Stereodrawings of the Cu₉Al₄ structure. The thermal ellipsoids show the calculated r.m.s. amplitudes of vibration of the atoms. The spokes join symmetry-related atoms, except those in the octahedral point complexes, and are not to be confused with bonds. (a) Cluster *A*, around the origin; 0,0,0; of the unit cell. The atoms are IT (inner tetrahedron): Al, OT (outer tetrahedron): Cu, OH (octahedron): Cu, CO (cubo-octahedron): Cu. (b) Cluster *B*, around $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; of the unit cell. The atoms are IT (inner tetrahedron): Cu, OT (outer tetrahedron): Cu, OH (octahedron): Cu, CO (cubo-octahedron): Al.

Table 1. *Refined structural parameters of Cu₉Al₄*

Estimated standard deviations are given in parentheses in units of the last significant figure.

Space group = $P\bar{4}3m$
 $a = 8.7068$ (3) Å
 $R = 2.4\%$

	Cluster A	Cluster B
	Al	Cu
IT 4(e) xxx	$x = 0.1157$ (6)	$x = 0.6066$ (3)
Inner tetrahedron	$b_{11} = 0.0019$ (4)	$b_{11} = 0.0044$ (3)
	$b_{12} = 0.0008$ (7)	$b_{12} = 0.0014$ (4)
	Cu	Cu
OT 4(e) xxx	$x = -0.1704$ (4)	$x = 0.3253$ (4)
Outer tetrahedron	$b_{11} = 0.0022$ (2)	$b_{11} = 0.0023$ (2)
	$b_{12} = 0.0005$ (3)	$b_{12} = 0.0000$ (3)
	Cu	Cu
OH 6(g) 00z	$z = 0.3553$ (5)	$z = 0.8549$ (5)
Octahedron	$b_{11} = 0.0023$ (3)	$b_{11} = 0.0035$ (3)
	$b_{33} = 0.0025$ (6)	$b_{33} = 0.0013$ (6)
	$b_{12} = 0.0006$ (5)	$b_{12} = 0.0008$ (5)
	Cu	Al
CO 12(i) xxx	$x = 0.3153$ (2)	$x = 0.8113$ (4)
Cubo-octahedron	$z = 0.0322$ (3)	$z = 0.5332$ (6)
	$b_{11} = 0.0041$ (3)	$b_{11} = 0.0032$ (5)
	$b_{33} = 0.0032$ (5)	$b_{33} = 0.0020$ (9)
	$b_{12} = -0.0004$ (3)	$b_{12} = 0.0004$ (6)
	$b_{13} = -0.0010$ (2)	$b_{13} = -0.0001$ (4)

The refinement described above and the subsequent tests for coherent twinning have all been based on traditionally screened intensity data: the 114 'reliable' independent reflections with $\sigma(I)/I > 0.16$. When we carried out yet another refinement using the entire data material, *i.e.* all the 150 measured $|F|^2$'s, we obtained a set of structural parameters without any significant change from that obtained earlier. The R value of course increased, from 2.44 to 3.78%, but most standard deviations of the parameters actually decreased slightly; the others remained constant.

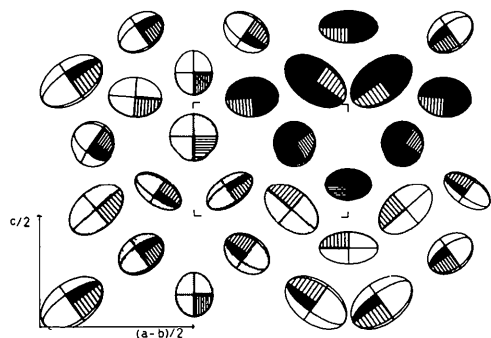


Fig. 2. Thermal ellipsoids scaled to $3\times$ the r.m.s. amplitudes of vibration of the atoms in the $(1\bar{1}0)$ plane through the origin of the Cu_9Al_4 unit cell. Clusters A and B are shown with lighter and darker shading, respectively, of the atoms. Indicated on the figure are the vectors $\frac{1}{2}(a-b)$ and $\frac{1}{2}c$.

It is quite clear that a measured value of $|F| \approx 0$ for a low-angle reflection carries as much information as any other, finite, value. The usual procedure of discarding all reflections for which $\sigma(I)/I$ exceeds some chosen limit may therefore be considered crystallographic malpractice. This question will be the subject of a forthcoming article.

Discussion of the refinement

The position parameters obtained in the present refinement do not differ much from those given by Heidenstam, Johansson & Westman (1968), but the precision is better by a factor of ~ 2 in the standard deviations. $\text{Cu}_{\text{IT}(B)}$ (for nomenclature see Table 1) has been shifted the most from its old position – by $\sim 3\sigma$ of that determination. Consequently, the calculated interatomic distance most significantly affected by the redetermination is $\text{Cu}_{\text{IT}(B)}-\text{Cu}_{\text{IT}(B)}$, which has increased from 2.574 (14) to 2.622 (9) Å. The change is unremarkable, in that the distance is still quite normal for a Cu–Cu contact.

At the same time, however, the thermal ellipsoid of $\text{Cu}_{\text{IT}(B)}$ has become real; it is now, in fact, the largest in the structure model. One possible interpretation of this observation is that IT(B) may be the site of substitution of Al for Cu upon increase of the phase's Al content. According to, unfortunately low-quality, data on rhombohedral Cu_8Al_5 (Lindahl & Westman, 1967) this seems to be the principal site for more Al to enter the structure. An attempt to refine a structure model with 3.5 atoms of Cu and 0.5 atoms of Al at IT(B), to match the stoichiometry indicated by the lattice parameter, resulted in slight increases of R and of the standard deviations of all structure parameters. Present data thus apparently refute the hypothesis.

The thermal vibrations of the IT and OT atoms might be expected to be directed mainly towards the 'vacancies' at 0,0,0; and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. This is clearly seen to be the case for cluster A (*cf.* Fig. 2). In cluster B , however, only the remarkably large oscillations of $\text{Cu}_{\text{IT}(B)}$ are so oriented, whereas $\text{Cu}_{\text{OT}(B)}$ is seen to vibrate isotropically.

It may finally be remarked that the shortest interatomic distances in the structure have turned out even shorter than in the older determination, although not significantly so: $\text{Cu}_{\text{CO}(A)}-\text{Cu}_{\text{OH}(B)} = 2.479$ (3) instead of 2.482 (8) Å, and $\text{Cu}_{\text{OT}(B)}-\text{Al}_{\text{CO}(B)} = 2.473$ (5) instead of 2.487 (14) Å.

Test of 'coherent twinning'

One hypothesis concerning the nature of the domains in Cu_9Al_4 observed by Gabriel Torres & Radcliffe (1975) is that they might represent antiphase domains. At the domain boundaries the structure could be shifted by

$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; or possibly inverted in the origin, to mention two clear-cut models. If the domains scatter coherently, the diffraction effects would simulate a 'more body-centred' and a 'more centrosymmetric' structure, respectively, in the two cases mentioned.

Test calculations of structure factors for different degrees of superposition of structure + shifted counterpart and of structure + inverse yielded the results summarized in Table 2. Less than 1% of twinning could obviously not be detected in this fashion with the data available, but above the 1% level the R values increase significantly for both models. Thus, at most 1% of twinning, of either kind, may reasonably be assumed to occur in the crystal.

If any of the atomic positions were split in two, and each half partially occupied, this would be another possibility for domains to differ in structure though not in composition. One obvious candidate for such splitting is the IT(B) atom, which our refinement appears to show oscillating with a relatively large

amplitude along [111]. Another possibility has been suggested by Brandon, Brizard, Chieh, McMillan & Pearson (1974), namely the OH atoms being tilted out from [110] to lean more closely against either of the two neighbouring OT atoms. Still another mode of distortion may be reasonably conceived: the CO atom leaving the (110) mirror plane to approach one of the two OH neighbours.

All these possibilities have been tried. The refinements of split-atom models all converged back to the higher-symmetry structure or diverged completely, depending on the initial distortion assumed. This type of model for disorder or coherent twinning is therefore also apparently ruled out by our data.

Test of 'incoherent twinning'

One further possibility would be that any domains present are incoherent, approximately aligned mosaic blocks, and that the structure in some blocks is inverted with respect to the others. In that case hkl reflections from one set of blocks would overlap the corresponding $\bar{h}\bar{k}\bar{l}$ reflections from the other set. This hypothesis was tested by means of measurement of the anomalous dispersion effect for the ten selected reflections recorded with Mo $K\alpha$ radiation.

In Table 3 we have compared the measured effect, $\Delta_o = |F_o(+)| - |F_o(-)|$, with that calculated for an ideal single crystal, $\Delta_c = |F_c(+)| - |F_c(-)|$. The quite

Table 2. Refinement results for 'coherent twin' models

Degree of twinning (% of crystal)	R value, %, for inverse structure	R value, %, for shifted structure
0	2.45	2.45
1	2.46	2.48
2	2.59	2.65
3	2.80	2.91
10	6.53	3.73

Table 3. Observed and calculated anomalous dispersion effects for 0 and 15% 'incoherent twinning'

$$\Delta = |F(+)| - |F(-)|.$$

hkl	$ F_o $	$ F_c (0\%)$	$ F_c (15\%)$	Δ_o	$\Delta_c(0\%)$	$\Delta_c(15\%)$
$\bar{1}45$	46.3	46.2	46.6	-1.7	-2.2	-1.4
$\bar{1}4\bar{5}$	48.0	48.4	48.0			
$\bar{1}18$	31.5	29.8	30.5	-3.6	-3.6	-2.3
$\bar{1}\bar{1}8$	35.1	33.4	32.8			
$\bar{2}28$	79.3	78.1	78.6	-2.7	-2.6	-1.7
$\bar{2}\bar{2}8$	82.0	80.7	80.3			
$\bar{1}38$	45.6	46.1	45.4	+2.3	+3.5	+2.2
$\bar{1}\bar{3}8$	43.3	42.6	43.2			
$\bar{2}68$	59.0	59.0	59.4	-1.4	-2.6	-1.8
$\bar{2}\bar{6}8$	60.4	61.6	61.2			
$\bar{1}78$	49.0	49.2	48.7	+3.0	+3.1	+2.0
$\bar{1}\bar{7}8$	46.0	46.1	46.7			
$\bar{3}69$	151.2	152.6	152.9	-1.3	-1.9	-1.3
$\bar{3}\bar{6}9$	152.5	154.5	154.2			
$\bar{4}410$	151.5	152.7	152.1	+2.6	+3.4	+2.2
$\bar{4}\bar{4}\bar{1}0$	148.9	149.3	149.9			
$\bar{1}710$	119.1	118.5	118.1	+2.5	+2.1	+1.3
$\bar{1}\bar{7}\bar{1}0$	116.6	116.4	116.8			
$\bar{3}312$	80.3	80.2	80.8	-3.0	-3.4	-2.2
$\bar{3}\bar{3}\bar{1}2$	83.3	83.6	83.0			
$R =$		0.939%	0.927%	$R_\Delta =$	22%	27%

remarkable correspondence between the two sets of quantities indicates that the crystal is essentially one individual, without significant twinning of the kind described above. Indeed, assuming a fraction, q , of incoherent inverse domains to be present, one calculates a set of corrected $|F_c|^2$ values: $|F_c(+, \text{corr.})|^2 = |F_c(+)|^2 - q[|F_c(+)|^2 - |F_c(-)|^2]$, and $|F_c(-, \text{corr.})|^2 = |F_c(-)|^2 + q[|F_c(+)|^2 - |F_c(-)|^2]$; a least-squares calculation of q , then, from the data in Table 3 yields $q = 0.15 \pm 0.07$. As seen from the table, however, R improves very little: from 0.939 to 0.927. A Hamilton test of the ratio $\mathcal{R}_0 = 0.939/0.927 = 1.013$ leads to rejection, with more than 50% probability, of the hypothesis that this is a real observation of 15% incoherent inverse domains; for $\mathcal{R}_0 = 1.013$ is much less than $\mathcal{R}_{1,10,0.50} = 1.024$. Furthermore, the quantity that could be designated

$$R_{\Delta} = \frac{100 \sum \left(|F_o(+)| - |F_o(-)| - \left| |F_c(+)| - |F_c(-)| \right| \right)}{\sum \left(|F_o(+)| - |F_o(-)| \right)}$$

actually increases from 22 to 27% when q is changed from 0 to 0.15.

It is obvious, of course, that occurrence of this type of twinning should be of no consequence whatsoever for the precise refinement of γ -brass or similar structures.

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A Method of Eliminating the Polarization Ratio of a Crystal Monochromator as an Interactive Constant in the Polarization Factor

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Disposition of a monochromator crystal relative to the specimen crystal on a diffractometer, such that the respective diffraction planes are at 45° , makes knowledge of the actual value of the polarization ratio for the monochromator crystal unnecessary for the conversion of measured intensities to structure-factor values for the specimen crystal. This arrangement, therefore, avoids the uncertainty often associated with poor knowledge of the polarization ratio of monochromator crystals, and so can contribute to improved accuracy of measured structure factors.