The Crystal Structure of GdAg$_{3.6}$*

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The crystal structure of the intermetallic phase GdAg$_{3.6}$ has been determined using three-dimensional diffractometer data from three different crystals. The space group is $P6/m$, with lattice parameters $a=12.670$ and $c=9.332$ Å. One disordered silver set is partially occupied. The range of stoichiometry of the phase is thought to be quite limited, corresponding to approximately 50% occupancy of the disordered set (X-ray density$=9.86$ g.cm^{-3}). On the basis of the very close correlation of the lattice parameters, this phase, common to many of the rare-earth–silver systems, likely defines the structure of the previously reported phase PuAg$_3$.

Introduction

The silver-rich phases of the RE–silver equilibrium systems (RE$=$Y, La, Ce, Sm, Gd, Dy, Ho, Er) were investigated by Steeb, Godel & Löhr (1968) who report on the basis of X-ray powder data, these phases to be isotypes of the phase PuAg$_3$,† found by Runnalls (1956). McMasters, Gschneidner & Venteicher (1970) found metallographic evidence of two phases at this composition and report the formula RE$_2$Ag$_7$ (RE$=$La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Y). On the basis of the very close agreement in the hexagonal lattice parameters reported by the two sets of investigators it appears likely that both have indeed investigated the same intermetallic phases. The present investigation was undertaken as an adjunct to the work of McMasters *et al.* in an attempt to detail the structure and thus resolve the uncertainty in the stoichiometry of the phase.

Experimental procedure

Single crystals from sample preparations of nominal stoichiometries GdAg$_5$, GdAg$_{3.5}$, ErAg$_{3.5}$ and LaAg$_3$ were provided by McMasters *et al.* and were examined by Weissenberg and precession X-ray techniques. In every case $6/m$ diffraction symmetry was observed. Contrary to the observations of Steeb *et al.* for REAg$_3$ and of Runnalls for PuAg$_3$, weak reflections of the type 00*l* with $l\neq2n$ were observed. Thus the probable space groups are $P6$, $P\bar{6}$ and $P6/m$. Diffractometric intensity data were collected from three different single crystals using zirconium filtered Mo $K\alpha$ radiation ($\lambda=0.7107$ Å).

(1) 1800 data were collected, yielding 589 observed data, from a small ($\sim7\times10^{-5}$ mm^3) regular crystal of nominal stoichiometry GdAg$_3$ by the 2θ scan technique using a General Electric single-crystal orienter

equipped with a scintillation counter. No formal absorption corrections were applied to the data. However, a correction was made for the sinusoidal variation of the intensity with φ caused by the Pyrex mounting fiber passing through the beam path.

(2) 2400 data were recorded in a quadrant of the reflecting sphere out to $\theta=25°$ from a crystal of nominal stoichiometry GdAg$_5$ by the 2θ scan technique using an automated Hilger–Watts four-circle diffractometer. The φ dependence of the 00*l* reflections measured at $\chi=90°$ was slight. The equivalent reflections were averaged to yield 818 unique data and no absorption corrections were applied. Lattice parameters $a_0=12.671\pm0.003$ Å and $c_0=9.333\pm0.003$ Å were computed by a least-squares fit to the Nelson–Riley (1945) function.

(3) 2640 data were recorded from half the reflecting sphere out to $\theta=20°$ from a crystal of nominal stoichiometry GdAg$_{3.5}$ in the same manner as for crystal 2. This crystal had the approximate form of a triangular pyramid $0.16\times0.12\times0.12$ mm along the edges of the base and with altitude 0.65 mm. Absorption corrections were computed with the program of Busing & Levy (1957) and after correction, the equivalent data were averaged to yield 439 unique data. Lattice parameters $a_0=12.670\pm0.003$ and $c_0=9.332\pm0.002$ Å were obtained as for crystal 2.

Structure determination

The data from crystal 3 were subjected to the statistical analysis of Howells, Phillips & Rogers (1950). This analysis clearly indicated the presence of a center of symmetry. Accordingly, a trial structure containing 14 Gd and 49 Ag atoms was chosen in space group $P6/m$ with the aid of a Patterson synthesis. Refinement of the trial structure was by the full-matrix least-squares program of Busing, Martin & Levy (1962). The atomic scattering factors of Cromer & Waber (1965) were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1962). Unit weights were applied in the early stages of refinement.

Table 1. Final parameters

E.s.d.'s are given in parentheses.

Atom	Wyckoff notation	x	y	z	β_{11}‡	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Gd(1)	2(e)	0	0	0·3060 (3)	0·0011 (1)	0·0011	0·0035 (3)	0·0005	0	0
Gd(2)	6(j)	0·3898 (1)	0·1138 (1)	0	0·0049 (2)	0·0019 (2)	0·0027 (2)	0·0021 (1)	0	0
Gd(3)	6(k)	0·1394 (1)	0·4680 (1)	½	0·0016 (2)	0·0010 (1)	0·0023 (2)	0·0005 (1)	0	0
Ag(1)	2(c)	⅓	⅔	½	0·0019 (2)	0·0019	0·0034 (5)	0·0010	0	0
Ag(2)	4(h)	⅓	⅔	0·2987 (3)	0·0014 (2)	0·0014	0·0040 (3)	0·0007	0	0
Ag(3)	6(k)	0·2383 (2)	0·0589 (2)	¼	0·0012 (2)	0·0012 (2)	0·0040 (4)	0·0007 (2)	0·0004 (2)	0·0002 (2)
Ag(4)	12(l)	0·2662 (1)	0·1918 (1)	0·2370 (2)	0·0018 (1)	0·0016 (1)	0·0036 (2)	0·0007 (1)	0·0002 (2)	0·0003 (2)
Ag(5)	12(l)	0·1155 (1)	0·4944 (1)	0·1526 (2)	0·0022 (1)	0·0011 (1)	0·0042 (3)	0·0007 (1)	0·0002 (1)	0·0005 (2)
Ag(6)	12(l)	0·4390 (1)	0·1049 (1)	0·3305 (2)	0·0014 (1)	0·0019 (2)	0·0050 (2)	0·0007 (1)	0	0
Ag(*)†	6(j)	0·1131 (5)	0·1324 (4)	0	0·0049 (6)	0·0016 (5)	0·0019 (7)	0·0018 (5)	0	0

† The set Ag* is partially occupied.
‡ Anisotropic temperature factors of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl + 2\beta_{23}kl + 2\beta_{12}hk)]$.

During the final stages other weighting schemes were applied. The refined parameters did not vary outside their standard deviations, nor did the residual vary more than 0·002 regardless of the weighting scheme used. All parameters reported herein are those achieved with unit weights.

During the course of the refinement several major adjustments, such as interchanging atomic species occupying specific sites, were made to the initial trial structure. These changes were made on the basis of the simultaneous consideration of difference syntheses, interatomic distances and the behavior of the isotropic temperature factors. By combination of least-squares refinement and such adjustments to the model the residual was rapidly reduced from the initial value 0·59 to 0·13. At this stage, on the basis of the difference synthesis, the origin atom was removed. The residual

Table 2. Observed and calculated structure factors

immediately dropped to 0·097, but new peaks in the difference synthesis indicated the need for an additional sixfold atom set near the origin with approximately 19–23 electrons at each site. The addition of a partially occupied set of silver atoms yielded a residual of 0·063 after refinement of the occupancy factor to 0·4742. Further refinement with anisotropic temperature factors, holding the occupancy factor fixed,

yielded 0·045 for the residual for the 439 reflections obtained from crystal 3.

No significant shift in any of the parameters was obtained by attempting further refinement in the noncentric space groups. The refined parameters are given in Table 1. The observed and calculated structure factors are compared in Table 2. The trial structure was also refined with data from crystals 1 and 2 with

Table 3. *Interatomic distances in* GdAg₃.₆

Atom	Ligand	Distance	Atom	Ligand	Distance
Gd(1)	1 Gd(1)	3·62 Å	Ag(4)	1 Gd(1)	3·08 Å
	6 Ag(3)	3.27		1 Gd(2)	3·14
	6 Ag(4)	3·08		1 Gd(2)	3·30
	'6 Ag*	3·26		1 Gd(3)	3·34
				1 Ag(3)	2·87
Gd(2)	1 Ag(1)	3·21		1 Ag(3)	2·90
	2 Ag(4)	3·14		2 Ag(4)	3·01
	2 Ag(4)	3·30		1 Ag(5)	2·78
	2 Ag(5)	3·18		1 Ag(6)	2·94
	2 Ag(5)	3·25		1 Ag(6)	3·03
	2 Ag(5)	3·26		'1 Ag*	2·79
	2 Ag(6)	3·16		'1 Ag*	2·97
	'1 Ag*	2·86		'1 Ag*	3·92
	'1 Ag*	3·63			
			Ag(5)	1 Gd(2)	3·17
Gd(3)	2 Ag(2)	3·12		1 Gd(2)	3·25
	1 Ag(3)	3·19		1 Gd(2)	3·26
	2 Ag(4)	3·34		1 Gd(3)	3·29
	2 Ag(5)	3·29		1 Ag(1)	2·90
	2 Ag(6)	3·10		1 Ag(2)	2·87
	2 Ag(6)	3·12		1 Ag(4)	2·78
	2 Ag(6)	3·17		1 Ag(5)	2·85
	1 Ag(3)	3·24		1 Ag(5)	3·00
Ag(1)	3 Gd(2)	3·21		1 Ag(6)	2·79
	2 Ag(2)	2·79		1 Ag(6)	3·00
	6 Ag(5)	2·90		1 Ag(6)	3·59
Ag(2)	3 Gd(3)	3·12	Ag*	2 Gd(1)	3·26
	1 Ag(1)	2·79		1 Gd(2)	2·86
	1 Ag(2)	3·76		1 Gd(2)	3·63
	3 Ag(5)	2·87		2 Ag(4)	2·76
	3 Ag(6)	2·90		2 Ag(4)	2·97
				2 Ag(4)	3·92
Ag(3)	2 Gd(1)	3·27		'2 Ag*	1·57
	1 Gd(3)	3·19		'2 Ag*	2·72
	1 Gd(3)	3·24		'1 Ag*	3·14
	2 Ag(4)	2·87			
	2 Ag(4)	2·90			
	2 Ag(6)	2·80			
	2 Ag(3)	2·72			
Ag(6)	1 Gd(2)	3·16			
	1 Gd(3)	3·10			
	1 Gd(3)	3·12			
	1 Gd(3)	3·17			
	1 Ag(2)	2·91			
	1 Ag(3)	2·80			
	1 Ag(4)	2·94			
	1 Ag(4)	3·03			
	1 Ag(5)	2·79			
	1 Ag(5)	3·00			
	1 Ag(5)	3·56			
	1 Ag(6)	3·16			
	1 Ag(6)	3·68			

' The multiplicity of bonds marked ' is dependent on the degree of occupancy of the Ag* set.

final residuals 0·139 and 0·067 respectively. The refined positional parameters obtained were within the standard deviations given in Table 1 for crystal 3. The section of the electron density synthesis at $z=0$ is shown in Fig. 1.

Discussion

The presence of a partially filled set in the structure implies a theoretical range of stoichiometry for the phase varying from $GdAg_{3·43}$ to $GdAg_{3·86}$ (0 to 100% occupancy of the Ag* set in Table 1). Examination of the interatomic distances given in Table 3 shows that the distance between adjacent sites in the partially filled set is much too small (1·57 Å) to permit simultaneous occupancy. Placing silver atoms in alternate sites, forming a triad, results in acceptable silver–silver bonds (2·72 Å). The occurrence of such triads with orientation varying randomly from cell to cell is likely
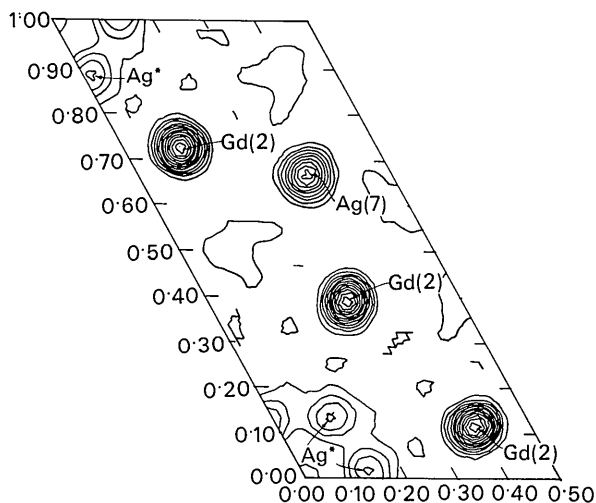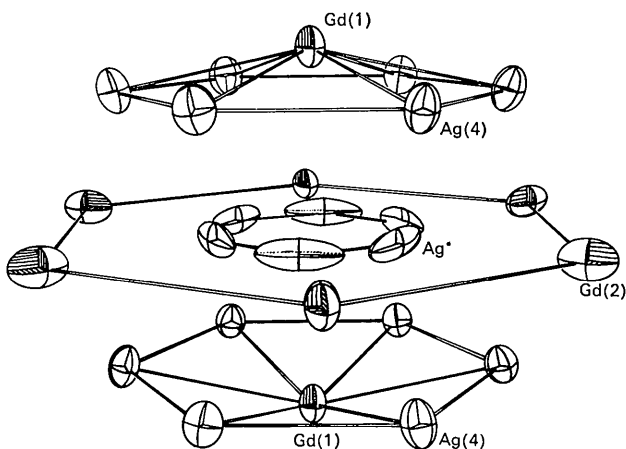

Fig. 1. Electron density section at $z=0$.

in the silver-rich limit of the stoichiometry of the phase, with occupancy factor 0·5 and stoichiometry $GdAg_{3·64}$.

There is one extremely short bond distance in the structure between each Gd(2) atom and the adjacent partially filled Ag* site (2·86 Å). This constriction can be somewhat relieved by a shift of the Gd(2) atom away from the Ag* site when occupied and a corresponding collapse back toward the site when empty. The thermal ellipsoids plotted in Fig. 2 support this mechanism and further suggest that the silver atoms in the Ag* site may also shift somewhat to alleviate the shortness of the bond.

The experimental occupancy factor for the Ag* site for crystal 3 corresponds to the stoichiometry $GdAg_{3·62}$. The values found for crystals 1 and 2 were higher, corresponding to $GdAg_{3·70\pm0·04}$ and $GdAg_{3·68\pm0·02}$ respectively. Due to the lack of absorption corrections to the data from these crystals and the consequent loss of precision in the refinement, these values may not be directly comparable with that of crystal 3. However they reflect a trend toward substantial occupancy of the partially filled atom set regardless of the nominal alloy stoichiometry. Attempts to directly analyse the experimental crystals with an electron microprobe failed owing to the problems of handling such very small samples. An analysis of a larger single crystal, nominally $GdAg_3$, indicated the stoichiometry $GdAg_{3·78\pm0·15}$. While the lack of precision of the analysis renders it inconclusive, when combined with the above observations it tends to further support the contention that the occupancy of the partially filled Ag* set remains close to the maximum and the range of stoichiometry of the phase is probably quite limited.

Fig. 2. Thermal ellipsoids of atoms near the origin. The set Ag* is partially occupied.

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