CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.

CRUICKSHANK, D. W. J. & SPARKS, R. A. (1960). *Proc. Roy. Soc.* A**258**, 270.

DHAR, J. (1932). *Indian J. Phys.* **7**, 43.

DALY, J. J., STEPHENS, F. S. & WHEATLEY, P. J. (1963). Monsanto Research S.A. Final Report No.52.

DEWAR, M. J. S. & SCHMEISING, H. N. (1959). *Tetrahedron*, **5**, 166.

FERGUSON, G. & SIM, G. A. (1961). *Acta Cryst.* **14**, 1262.

HARGREAVES, R. & RIZVI, S. H. (1962). *Acta Cryst.* **15**, 365.

*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.

SUTHERLAND, H. H. (1969). *Acta Cryst.* B**25**, 171.

SUTHERLAND, H. H. & HOY, T. G. (1968). *Acta Cryst.* B**24**, 1207.

SUTHERLAND, H. H. & HOY, T. G. (1969). *Acta Cryst.* B**25**, 1013.

TROTTER, J. (1961). *Acta Cryst.* **14**, 1135.

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

# Crystallography of the Silver-Rich Rare-Earth–Silver Intermetallic Compounds

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The crystal structures of the silver-rich compounds in the rare-earth–silver systems were determined by means of X-ray powder diffraction methods. Metallographic methods were used to confirm the stoichiometries. The low temperature form of LaAg$_5$ crystallizes in a 'substituted' MgZn$_2$ ($C14$) type Laves-phase structure. The high temperature polymorph of LaAg$_5$ and the phases CeAg$_5$, PrAg$_5$ and YbAg$_5$ were found to be isotypic but the crystal structure was not established. EuAg$_5$ crystallizes in the CaCu$_5$ ($D2_d$) type structure; LuAg$_4$ and ScAg$_4$ of the MoNi$_4$ ($D1_a$) type were found. $R_{14}$Ag$_{51}$ phases of the Gd$_{14}$Ag$_{51}$ type exist for $R=$Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er. Yb$_2$Ag$_7$ crystallizes in the Ca$_2$Ag$_7$ type structure. TmAg$_3$ was found to exist in both the AuCu$_3$ ($L1_2$) type and the TiCu$_3$ ($D0_a$) type structures. The crystallographic data for these phases are given and their structural relationships are discussed.

## Introduction

During an investigation of the solubility limits of the rare earths in silver, it became necessary to determine the stoichiometry of the first silver-rich compound in the rare-earth–silver systems (Gschneidner, McMasters, Alexander & Venteicher, 1970). Since most of these compounds are new, their structural properties and crystallographic data were determined and are the subject of this paper.

All of the rare earths except europium form the $R$Ag compound with the cubic CsCl ($B2$) type structure. These phases have been studied by several investigators and most of their results are given in Pearson (1967) and McMasters & Gschneidner (1964). For YbAg and YAg the data are given by Moriarty, Humphreys, Gordon & Baenziger (1966). Iandelli & Palenzona (1969) have shown that YbAg crystallizes in both the CsCl and FeB type structures. Köster & Meixner (1965) reported that EuAg exists but the structure was not established.

For $R=$La, Ce, Pr, Nd, Eu and Yb the phase $R$Ag$_2$ crystallizes in the orthorhombic CeCu$_2$ (KHg$_2$) type structure according to Iandelli & Palenzona (1968) and Köster & Meixner (1965) in the case of EuAg$_2$. For $R=$Gd, Tb, Dy, Ho, Er, Tm, Lu, Sc and Y the

$R$Ag$_2$ phase of the tetragonal MoSi$_2$ ($C11_b$) type structure has been reported by several investigators: Baenziger & Moriarty (1961), Moriarty, Gordon & Humphreys (1965), Dwight, Downey & Conner (1967), Kusma & Laube (1965), Ferro, Capelli, Borsese & Delfino (1967), Iandelli & Palenzona (1968), and Steeb, Godel & Lohr (1968). Different structures have been reported for SmAg$_2$ by Iandelli & Palenzona (1968), for YbAg$_2$ by Moriarty, Humphreys, Gordon & Baenziger (1966), and for YAg$_2$ by Gebhardt, von Erdberg & Lütz (1964).

The structure data for the $R$Ag$_3$ phases reported by Steeb, Godel & Lohr (1968) and Donalato & Steeb (1969) will be discussed later in connection with results of our investigation.

Lattice parameters and structure types for Yb$_5$Ag$_3$ (Cr$_5$B$_3$ type) and Yb$_3$Ag$_2$ (U$_3$Si$_2$ type) were determined by Iandelli & Palenzona (1969). Palenzona (1967) and Köster & Meixner (1965) reported EuAg$_5$ as being of the hexagonal CaCu$_5$ ($D2_d$) type structure. The latter also reported that the phases EuAg$_4$ and Eu$_5$Ag$_3$ exist but did not determine the structures.

## Experimental procedures

The purity of the metals used in this investigation and alloy preparation procedures are described by Gschnei-

dner *et al.* (1970). Samples, weighing 5–8 g, of the stoichiometries $RAg_6$, $RAg_5$, $RAg_4$, $R_2Ag_7$, and $RAg_3$ were prepared for most of the R–Ag systems by arc-melting techniques. For $R = Eu$ and Yb the samples were prepared by induction heating the constituents in sealed tantalum crucibles. Weight losses were found to be negligible and heat treatments were carried out with the alloys sealed in tantalum crucibles. All samples were examined by metallographic and X-ray powder techniques. The metallographic results were used to confirm the compound stoichiometries and are given in detail by Gschneidner *et al.* (1970). The powder specimens were prepared under an inert gas atmosphere and were sealed in Pyrex capillaries for use in the X-ray analysis.

A computer program written by Yvon, Jeitschko & Parthé (1969) was used to interpret the powder patterns. The extrapolated lattice parameters were determined by a least-squares fit of the back-reflection powder pattern data and the Nelson–Riley function by means of a computer program written by Vogel & Kempter (1961). The calculated $\sin^2\theta$ values listed in the text are based on the extrapolated lattice parameters for the compounds and are therefore less than the observed $\sin^2\theta$ values since the latter contain the sample absorption error. The magnitude of the differences $(\sin^2\theta_c - \sin^2\theta_o)$ is reflected in the slope of the straight line obtained by the extrapolation program. The accuracy of the lattice parameters (reported $\sigma_s$) corresponds to the standard deviation calculated for the observed reflection data in reference to the fitted straight line. Both Cr $K\alpha$, $\lambda = 2\cdot29092$ Å $(\lambda_1 = 2\cdot28962$ and $\lambda_2 = 2\cdot29351$ Å) and Cu$K\alpha$, $\lambda = 1\cdot54178$ Å$(\lambda_1 = 1\cdot54050$ and $\lambda_2 = 1\cdot54434$Å) were used in conjunction with a 114·6 mm Debye–Scherrer camera.

## Results

Lattice parameters and structure types of the new rare-earth–silver compounds studied in this investigation are listed in Table 1.

$RAg_5$, 83·3 *at.%* Ag

The compounds $LaAg_5$, $CeAg_5$, $PrAg_5$, $YbAg_5$, and $EuAg_5$ were found to exist. The powder pattern data for the low temperature modification of $LaAg_5$ are given in Table 2. The sample which yielded this pattern had been heat treated at 500 °C for 2 weeks. The powder pattern was indexed on the basis of the $MgZn_2$ (C14) type Laves-phase structure and the agreement between the observed and calculated intensity and $\sin^2\theta$ data is excellent. This agreement is retained when the $AB_2$ stoichiometry is shifted to $AB_5$ by randomly substituting two Ag atoms for two La atoms per unit cell. It was therefore concluded that $LaAg_5$ crystallizes in a 'substituted' $MgZn_2$ (C14) type structure. The calculated pattern based on the $LuMn_5$ (prototype to C14) structure reported by Wang & Gilfrich (1966) accounts for the more intense reflections of the $LaAg_5$ pattern; however, several discrepancies between the calculated and observed less intense reflections occur. For this reason the $LuMn_5$ (C14) prototype structure was eliminated as a possible solution for this structure.

The powder pattern of the $LaAg_5$ sample that had been heat treated at 780 °C for 2 days contained several more reflections than that of the low temperature form but was not extremely complex. Attempts to index the pattern were unsuccessful, but it was determined that the structure is closely related to the low temperature form. This became apparent during the comparison of the observed $\sin^2\theta$ values with those calculated for the known Laves and Laves-related structures. The $b$ and $c$ type variations of the $CaCu_5$ type structure reported by Bronger (1967) for some $RPt_5$ phases could not be compared since the structural data are incomplete.

The $CeAg_5$, $PrAg_5$, and $YbAg_5$ phases are isostructural with the high temperature $LaAg_5$ phase as evidenced by the similarity in their powder patterns. Various heat treatments failed to produce these three $RAg_5$ compounds in the low temperature $LaAg_5$ crystalline form. The powder patterns of $PrAg_5$ and $YbAg_5$ are nearly identical and they probably have nearly the

Table 1. *Structure data for some rare-earth–silver binary intermetallic compounds*

| Compound | Crystal system | Space group | Structure type | Lattice constants | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | | | $a_0$ | $b_0$ | $c_0$ |
| $LaAg_5$ (low temp.) | hexagonal | $P6_3/mmc$ | 'substituted' $MgZn_2(C14)$ | $5\cdot5690 \pm 0\cdot0003$ Å | — | $9\cdot0775 \pm 0\cdot0005$ Å |
| $EuAg_5$ | hexagonal | $P6/mmm$ | $CaCu_5(D2_d)$ | $5\cdot6201 \pm 0\cdot0008$ | — | $4\cdot6439 \pm 0\cdot0008$ |
| $LuAg_4$ | tetragonal | $I4/m$ | $MoNi_4(D1_a)$ | $6\cdot6696 \pm 0\cdot0002$ | — | $4\cdot1581 \pm 0\cdot0002$ |
| $ScAg_4$ | tetragonal | $I4/m$ | $MoNi_4(D1_a)$ | $6\cdot5740 \pm 0\cdot0002$ | — | $4\cdot0686 \pm 0\cdot0008$ |
| $La_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot955 \pm 0\cdot005$ | — | $9\cdot525 \pm 0\cdot007$ |
| $Ce_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot883 \pm 0\cdot005$ | — | $9\cdot455 \pm 0\cdot008$ |
| $Pr_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot846 \pm 0\cdot003$ | — | $9\cdot446 \pm 0\cdot005$ |
| $Nd_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot814 \pm 0\cdot002$ | — | $9\cdot432 \pm 0\cdot006$ |
| $Sm_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot750 \pm 0\cdot003$ | — | $9\cdot381 \pm 0\cdot002$ |
| $Gd_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot681 \pm 0\cdot003$ | — | $9\cdot289 \pm 0\cdot004$ |
| $Tb_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot650 \pm 0\cdot005$ | — | $9\cdot280 \pm 0\cdot003$ |
| $Dy_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot635 \pm 0\cdot003$ | — | $9\cdot271 \pm 0\cdot002$ |
| $Ho_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot609 \pm 0\cdot006$ | — | $9\cdot257 \pm 0\cdot002$ |
| $Er_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot596 \pm 0\cdot002$ | — | $9\cdot236 \pm 0\cdot001$ |
| $Y_{14}Ag_{51}$ | hexagonal | $P6/m$ | $Gd_{14}Ag_{51}$ | $12\cdot637 \pm 0\cdot003$ | — | $9\cdot300 \pm 0\cdot002$ |
| $Yb_2Ag_7$ | hexagonal | $P6_322$ | $Ca_2Ag_7$ | $5\cdot463 \pm 0\cdot001$ | — | $14\cdot084 \pm 0\cdot005$ |
| $TmAg_3$ | cubic | $Pm3m$ | $AuCu_3(L1_2)$ | $4\cdot2117 \pm 0\cdot0005$ | — | — |
| $TmAg_3$ | orthorhombic | $Pmmn$ | $TiCu_3(D0_a)$ | $6\cdot075 \pm 0\cdot005$ | $4\cdot948 \pm 0\cdot002$ | $5\cdot163 \pm 0\cdot003$ |

Table 2. *Calculated and observed powder pattern data for LaAg5, low temperature form*

Cu $K\alpha$ radiation. Atomic scattering factors for atoms in the $4(f)$ $(\frac{1}{3},\frac{2}{3},z;$ *etc.*) positions are an average of $f_{La}$ and $f_{Ag}$.

LaAg5($C14$) MgZn2 type

| sin² $\theta_o$ | $I_o$ | h | k | l | sin² $\theta_c$ | $I_c$ |
|---|---|---|---|---|---|---|
| 0·0780 | ms | 1 | 1 | 0 | 0·0767 | 307 |
| 0·0919 | s | 1 | 0 | 3 | 0·0905 | 703 |
| 0·1035 | w | 2 | 0 | 0 | 0·1022 | 107 |
| 0·1070 | vs | 1 | 1 | 2 | 0·1055 | 1000 |
| 0·1108 | vs | 2 | 0 | 1 | 0·1094 | 816 |
| 0·1169 | mw | 0 | 0 | 4 | 0·1154 | 184 |
| 0·1327 | mw | 2 | 0 | 2 | 0·1310 | 162 |
| 0·1430 | mw | 1 | 0 | 4 | 0·1409 | 100 |
| 0·2327 | w | 3 | 0 | 0 | 0·2299 | 57 |
| 0·2454 | ms | 2 | 1 | 3 | 0·2438 | 274 |
| 0·2606 | ms | 3 | 0 | 2 | 0·2588 | 244 |
| 0·2843 | ms | 2 | 0 | 5 | 0·2843 | 313 |
| 0·2962 | w | 2 | 1 | 4 | 0·2942 | 80 |
| 0·3086 | ms | 2 | 2 | 0 | 0·3066 | 274 |
| 0·3634 | m | 2 | 0 | 6 | 0·3618 | 116 |
| 0·3990 | m | 3 | 1 | 3 | 0·3970 | 133 |
| 0·4174 | m | 4 | 0 | 1 | 0·4160 | 95 |
| 0·4235 | m | 2 | 2 | 4 | 0·4220 | 136 |
| 0·4399 | mw | 2 | 1 | 6 | 0·4385 | 21 |
|  |  | 4 | 0 | 2 | 0·4376 | 23 |
| 0·4494 | w | 3 | 1 | 4 | 0·4475 | 31 |
| 0·4577 | w | 2 | 0 | 7 | 0·4556 | 25 |
| 0·4882 | w | 1 | 0 | 8 | 0·4871 | 45 |
| 0·5392 | w | 4 | 1 | 0 | 0·5365 | 32 |
|  |  | 1 | 1 | 8 | 0·5382 | 32 |
| 0·5527* | m | 3 | 2 | 3 | 0·5503 | 99 |

Table 2 (*cont.*)

| sin² $\theta_o$ | $I_o$ | h | k | l | sin² $\theta_c$ | $I_c$ |
|---|---|---|---|---|---|---|
| 0·5670 | s | 4 | 1 | 2 | 0·5654 | 156 |
|  |  | 2 | 2 | 6 | 0·5662 | 76 |
| 0·5908 | ms | 4 | 0 | 5 | 0·5891 | 114 |
| 0·6418 | m | 2 | 1 | 8 | 0·6404 | 88 |
| 0·6704 | mw | 4 | 0 | 6 | 0·6684 | 61 |
| 0·7048 | w | 5 | 0 | 3 | 0·7036 | 35 |
| 0·7204 | m | 3 | 3 | 2 | 0·7187 | 75 |
| 0·7240 | m | 4 | 2 | 1 | 0·7226 | 129 |
| 0·7459 | mw | 4 | 2 | 2 | 0·7442 | 34 |
|  |  | 3 | 2 | 6 | 0·7451 | 30 |
| 0·7437 | w | 2 | 1 | 9 | 0·7630 | 27 |
| 0·7951 | m | 3 | 1 | 8 | 0·7937 | 86 |
| 0·8244 | mw | 2 | 0 | 10 | 0·8234 | 77 |
| 0·8385 | w | 3 | 2 | 7 | 0·8388 | 49 |
| 0·8578 | ms | 5 | 1 | 3 | 0·8569 | 102 |
| 0·8964 | s | 4 | 2 | 5 | 0·8957 | 347 |
| 0·9078 | mw | 5 | 1 | 4 | 0·9074 | 50 |
| 0·9170 | mw | 3 | 1 | 9 | 0·9163 | 51 |
| 0·9205 | ms | 6 | 0 | 0 | 0·9198 | 200 |
| 0·9474 | mw | 3 | 2 | 8 | 0·9470 | 140 |
| 0·9752 | s | 2 | 0 | 11 | 0·9748 | 357 |
|  |  | 4 | 2 | 6 | 0·9750 | 401 |

\* Observed value consists of $K\alpha_1$ and $K\alpha_2$ converted to $K\alpha$ (mean) data in order to simplify the listing. This holds for values from asterisk to end of Table.

same lattice parameter values, which suggests that the Yb in this compound is divalent.

It is conceivable that the stoichiometry of these

Table 3. *Calculated and observed patterns of the tetragonal* MoNi4 ($D1_a$) *type structures of* LuAg4 *and* ScAg4

Cu $K\alpha$ (mean) radiation.

| LuAg4 $a_0=6\cdot6696$, $c_0=4\cdot1581$ Å |  |  |  |  |  |  | ScAg4 $a_0=6\cdot5740$, $c_0=4\cdot0686$ Å |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| sin² $\theta_o$ | $I_o$ | sin² $\theta_c$ | $I_c$ | h | k | l | sin² $\theta_o$ | $I_o$ | sin² $\theta_c$ | $I_c$ |
| — | — | 0·0267 | 26 | 1 | 1 | 0 | 0·0275 | w | 0·0275 | 49 |
| 0·0487 | vw | 0·0477 | 27 | 1 | 0 | 1 | 0·0504 | w | 0·0497 | 49 |
| 0·0527 | vw | 0·0534 | 12 | 2 | 0 | 0 | 0·0553 | w | 0·0550 | 21 |
| 0·1015 | vs | 0·1012 | 1000 | 1 | 2 | 1 | 0·1057 | vvs | 0·1047 | 1000 |
| 0·1334 | s | 0·1336 | 331 | 3 | 1 | 0 | 0·1385 | vs | 0·1375 | 331 |
| 0·1379 | s | 0·1375 | 158 | 0 | 0 | 2 | 0·1452 | s | 0·1436 | 154 |
| — | — | 0·1546 | 6 | 3 | 0 | 1 | 0·1603 | w | 0·1597 | 10 |
| — | — | 0·1642 | 5 | 1 | 1 | 2 | 0·1733 | vw | 0·1711 | 9 |
| 0·1915 | vw | 0·1909 | 4 | 2 | 0 | 2 | 0·2005 | vw | 0·1986 | 7 |
| 0·2082 | vw | 0·2080 | 7 | 3 | 2 | 1 | 0·2157 | w | 0·2147 | 13 |
| — | — | 0·2444 | 3 | 2 | 2 | 2 | 0·2549 | vw | 0·2536 | 5 |
| 0·2664 | ms | 0·2672 | 110 | 2 | 4 | 0 | 0·2769 | s | 0·2750 | 108 |
| 0·2707 | s | 0·2711 | 215 | 3 | 1 | 2 | 0·2832 | vs | 0·2811 | 209 |
| 0·3681 | s | 0·3684 | 256 | 5 | 0 | 1 | 0·3816 | vs | 0·3797 | 248 |
| 0·3752 | s | 0·3761 | 124 | 1 | 2 | 3 | 0·3935 | vs | 0·3919 | 118 |
| 0·4037 | s | 0·4047 | 111 | 2 | 4 | 2 | 0·4205 | vs | 0·4186 | 106 |
| — | — | 0·4218 | 2 | 2 | 5 | 1 | 0·4365 | vw | 0·4347 | 5 |
| — | — | 0·4830 | 2 | 2 | 3 | 3 | 0·5022 | w | 0·5019 | 4 |
| 0·5380 | w | 0·5344 | 39 | 6 | 2 | 0 | 0·5510 | m | 0·5500 | 38 |
| 0·5521 | w | 0·5499 | 19 | 0 | 0 | 4 | 0·5743 | mw | 0·5744 | 18 |
| — | — | 0·5917 | 1 | 5 | 3 | 2 | 0·6121 | w | 0·6111 | 4 |
| 0·6384* | m | 0·6355 | 71 | 3 | 6 | 1 | 0·6560 | m | 0·6547 | 72 |
| 0·6453 | ms | 0·6433 | 142 | 5 | 0 | 3 | 0·6684 | s | 0·6669 | 144 |
| 0·6705 | m | 0·6680 | 72 | 5 | 5 | 0 | 0·6900 | s | 0·6875 | 72 |
| 0·6743 | m | 0·6719 | 71 | 6 | 2 | 2 | 0·6946 | s | 0·6936 | 73 |
| 0·6860 | m | 0·6835 | 71 | 3 | 1 | 4 | 0·7130 | s | 0·7119 | 75 |
| 0·8071 | s | 0·8055 | 166 | 5 | 5 | 2 | 0·8321 | vs | 0·8311 | 176 |
| 0·8184 | s | 0·8171 | 86 | 2 | 4 | 4 | 0·8500 | vs | 0·8494 | 93 |
| 0·9035 | s | 0·9027 | 234 | 7 | 4 | 1 | 0·9300 | vs | 0·9297 | 274 |
| 0·9114 | s | 0·9105 | 122 | 3 | 6 | 3 | 0·9423 | vs | 0·9419 | 151 |
| 0·9267 | s | 0·9260 | 134 | 1 | 2 | 5 | 0·9664 | vs | 0·9663 | 199 |

\* See footnote for Table 2.

Table 5 (cont.)

| $\sin^2\theta_o$ | $I_o$ | h | k | l | $\sin^2\theta_c$ | $I_c$ |
|---|---|---|---|---|---|---|
| 0·9026 | mw | 9 | 0 | 1 | 0·9008 | 55 |
|  |  | 4 | 4 | 5 | 0·9057 | 45 |
| 0·9202 | w | 8 | 2 | 0 | 0·9183 | 90 |
| 0·9260 | ms | 7 | 3 | 2 | 0·9246 | 436 |
| 0·9329 | ms | 3 | 6 | 4 | 0·9325 | 291 |
| 0·9511 | m | 2 | 6 | 5 | 0·9494 | 118 |
| 0·9535 | s | 4 | 3 | 6 | 0·9530 | 123 |
|  |  | 2 | 3 | 7 | 0·9543 | 170 |
|  |  | 0 | 0 | 8 | 0·9751 | 129 |
| 0·9770 | s | 1 | 4 | 7 | 0·9761 | 229 |
|  |  | 7 | 2 | 4 | 0·9762 | 447 |

\* See footnote for Table 2.

Steeb, Godel & Lohr (1968) reported lattice parameters for some $RAg_3$ ($R$=La, Ce, Sm, Gd, Dy, Ho, Y and Er) compounds. For $R$=Pr, Nd, Tb and Tm the $RAg_3$ lattice parameters were reported by Donalato & Steeb (1969). Their lattice parameters are close to those of the $R_{14}Ag_{51}$ phases found in this study. It is believed that their $RAg_3$ lattice parameters are actually

for the $R_{14}Ag_{51}$ stoichiometry with the possibility of slight solubility ranges existing for these phases.

$Yb_2Ag_7$ crystallizes in the hexagonal $Ca_2Ag_7$ type

Table 6. *Calculated and observed powder patterns for* $Yb_2Ag_7$ *with the* $Ca_2Ag_7$ *type structure*

Cu Kα radiation.

| $I_o$ | $\sin^2\theta_o$ | h | k | l | $\sin^2\theta_c$ |
|---|---|---|---|---|---|
| w | 0·0483 | 0 | 0 | 4 | 0·0479 |
| m | 0·0539 | 1 | 0 | 3 | 0·0535 |
| s | 0·0755 | 1 | 0 | 4 | 0·0745 |
| m | 0·0804 | 1 | 1 | 0 | 0·0797 |
| s | 0·0832 | 1 | 1 | 1 | 0·0827 |
| m | 0·0921 | 1 | 1 | 2 | 0·0916 |
| s | 0·1022 | 1 | 0 | 5 | 0·1015 |
| vs | 0·1073 | 2 | 0 | 0 | 0·1062 |
|  |  | 1 | 1 | 3 | 0·1066 |
| m | 0·1186 | 2 | 0 | 2 | 0·1182 |
| m | 0·1278 | 1 | 1 | 4 | 0·1276 |
| m | 0·1328 | 2 | 0 | 3 | 0·1332 |
| m | 0·1361 | 1 | 0 | 6 | 0·1344 |
| m | 0·1880 | 1 | 1 | 6 | 0·1875 |
| w | 0·1935 | 0 | 0 | 8 | 0·1917 |
| m | 0·2150 | 2 | 0 | 6 | 0·2141 |

Table 7. *Calculated and observed powder patterns for* $TmAg_3$ *which exists in both the cubic* $AuCu_3$ *(L1$_2$) and the orthorhombic* $TiCu_3$ *(DO$_a$) type structures*

Cu Kα (mean) radiation.
$TmAg_3$ observed powder pattern 75 at.% Ag

| $I_c$ | $\sin^2\theta_c$ | h | k | l | $\sin^2\theta_o$ | $I_o$ | h | k | l | $\sin^2\theta_c$ | $I_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | 0·0885 | m | 2 | 0 | 1 | 0·0867 | 330 |
|  |  |  |  |  | 0·0910 | w | 0 | 0 | 2 | 0·0892 | 67 |
|  |  |  |  |  | 0·0982 | m | 0 | 2 | 0 | 0·0971 | 445 |
| 1000 | 0·1005 | 1 | 1 | 1 | 0·1024 | vs |  |  |  |  |  |
|  |  |  |  |  | 0·1072 | vw | 1 | 0 | 2 | 0·1053 | 10 |
|  |  |  |  |  | 0·1124 | s | 2 | 1 | 1 | 0·1110 | 1000 |
|  |  |  |  |  | 0·1154 | ms | 0 | 1 | 2 | 0·1134 | 607 |
| 489 | 0·1340 | 2 | 0 | 0 | 0·1356 | s |  |  |  |  |  |
|  |  |  |  |  | 0·1855 | mw | 2 | 2 | 1 | 0·1838 | 213 |
|  |  |  |  |  | 0·2605 | w | 4 | 0 | 0 | 0·2576 | 97 |
| 322 | 0·2680 | 2 | 2 | 0 | 0·2705 | vs | 2 | 0 | 3 | 0·2651 | 174 |
|  |  |  |  |  | 0·3076 | m | 2 | 3 | 1 | 0·3052 | 200 |
|  |  |  |  |  |  |  | 0 | 3 | 2 | 0·3076 | 124 |
|  |  |  |  |  | 0·3565 | w | 4 | 2 | 0 | 0·3547 | 114 |
|  |  |  |  |  |  |  | 0 | 0 | 4 | 0·3567 | 30 |
|  |  |  |  |  | 0·3641 | mw | 2 | 2 | 3 | 0·3621 | 209 |
| 381 | 0·3685 | 3 | 1 | 1 | 0·3704 | vs | 4 | 1 | 2 | 0·3711 | 183 |
| 111 | 0·4020 | 2 | 2 | 2 | 0·4039 | ms |  |  |  |  |  |
|  |  |  |  |  | 0·4458 | vw | 4 | 2 | 2 | 0·4439 | 22 |
|  |  |  |  |  | 0·4745 | vw | 2 | 4 | 1 | 0·4751 | 47 |
| 58 | 0·5360 | 4 | 0 | 0 | 0·5375\* | m |  |  |  |  |  |
| 213 | 0·6365 | 3 | 3 | 1 | 0·6390 | s | 4 | 1 | 4 | 0·6386 | 57 |
| 214 | 0·6700 | 4 | 2 | 0 | 0·6721 | m |  |  |  |  |  |
|  |  |  |  |  | 0·6939 | mw | 2 | 5 | 1 | 0·6935 | 84 |
|  |  |  |  |  | 0·7022 | w | 6 | 2 | 1 | 0·6991 | 39 |
|  |  |  |  |  | 0·7137 | mw | 4 | 2 | 4 | 0·7114 | 67 |
|  |  |  |  |  | 0·7366 | w | 4 | 4 | 2 | 0·7352 | 17 |
|  |  |  |  |  | 0·7832 | mw | 6 | 0 | 3 | 0·7803 | 66 |
| 253 | 0·8040 | 4 | 2 | 2 | 0·8055 | s | 0 | 0 | 6 | 0·8026 | 30 |
|  |  |  |  |  | 0·8223 | ms | 6 | 3 | 1 | 0·8204 | 104 |
|  |  |  |  |  | 0·8343 | m | 4 | 3 | 4 | 0·8328 | 74 |
|  |  |  |  |  | 0·8416 | m | 2 | 3 | 5 | 0·8402 | 160 |
|  |  |  |  |  | 0·8730 | w | 0 | 6 | 0 | 0·8738 | 46 |
|  |  |  |  |  | 0·8797 | s | 6 | 2 | 3 | 0·8774 | 178 |
| 488 | 0·9046 | 3 | 3 | 3 | 0·9053 | s | 0 | 2 | 6 | 0·8997 | 89 |
|  |  |  |  |  | 0·9525 | ms | 4 | 5 | 2 | 0·9536 | 292 |
|  |  |  |  |  | 0·9615 | mw | 2 | 6 | 1 | 0·9605 | 119 |

\* See footnote for Table 2.

Table 8. *Intermetallic compound formation in the rare-earth–silver systems*

Stoichiometry and structure differences yielding eight sequences.

| Sequence number | Rare earth | $R_5Ag_3$ | $R_3Ag_2$ | $RAg$ | $RAg_2$ | $RAg_3$ | $R_2Ag_7$ | $R_{14}Ag_{51}$ | $RAg_4$ | $RAg_5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | La, Ce, Pr | | | × | × * | | | × | | × † |
| 2 | Nd | | | × | × * | | | × | | |
| 3 | Sm | | | × | × † | | | × | | |
| 4 | Eu | × † | | × † | × * | | | | × † | × |
| 5 | Gd, Tb, Dy, Ho, Er, Y | | | × | × ‡ | | | × | | |
| 6 | Tm | | | × | × ‡ | × | | | | |
| 7 | Yb | × | × | × | × * | | × | | | × † |
| 8 | Lu, Sc | | | × | × ‡ | | | | × | |

\* $CeCu_2$, $KHg_2$ type.
† Structure type unknown.
‡ $MoSi_2$ type.

structure reported in Pearson (1958). The atomic parameters needed to calculate the powder pattern intensities are not known so the observed and calculated $sin^2\theta$ values listed for comparison in Table 6 are given as evidence for this structure.

## References

BAENZIGER, N. C. & MORIARTY, J. L. (1961). *Acta Cryst.* **14**, 948.

BAILEY, D. M. & KLINE, G. R. (1970). *Acta Cryst.* To be published.

BRONGER, W. (1967). *J. Less-Common Metals*, **12**, 63.

DONALATO, C. & STEEB, S. (1969). *J. Less-Common Metals*, **18**, 312, 442.

DWIGHT, A. E., DOWNEY, J. W. & CONNER, R. A. JR (1967). *Acta Cryst.* **22**, 745.

FERRO, R., CAPELLI, R., BORSESE, A. & DELFINO, S. (1967). *R. C. Accad. Lincei*, **42**, 60.

GEBHARDT, E., ERDBERG, M. VON & LÜTZ, U. (1964). *Nuclear Metallurgy*, **10**, 303.

GSCHNEIDNER, K. A. JR, MCMASTERS, O. D., ALEXANDER, D. G. & VENTEICHER, R. G. (1970). *Met. Trans.* **1**, 1961.

HARKER, D. (1944). *J. Chem. Phys.* **12**, 315.

IANDELLI, A. & PALENZONA, A. (1968). *J. Less-Common Metals*, **15**, 273.

IANDELLI, A. & PALENZONA, A. (1969). *Binary Phase Diagrams of Ytterbium with* Cu, Ag, Au. Paper presented at Colloques International du C.N.R.S. sur les Eléments der Terres Rares, Paris–Grenoble, May 5–10.

KÖSTER, W. & MEIXNER, J. (1965). *Z. Metallk.* **56**, 695.

KUSMA, J. B. & LAUBE, E. (1965). *Mh. Chem.* **96**, 1496.

MCMASTERS, O. D. & GSCHNEIDNER, K. A. JR (1964). *Nuclear Metallurgy*, **10**, 93.

MORIARTY, J. L., GORDON, R. O. & HUMPHREYS, J. E. (1965). *Acta Cryst.* **19**, 285.

MORIARTY, J. L., HUMPHREYS, J. E., GORDON, R. O. & BAENZIGER, N. C. (1966). *Acta Cryst.* **21**, 840.

PALENZONA, A. (1967). *R. C. Accad. Lincei*, **42**, 504.

PEARSON, W. B. (1958). *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 1. New York: Pergamon Press.

PEARSON, W. B. (1967). *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2. New York: Pergamon Press.

SADOGOPAN, V., GIESSEN, B. C. & GRANT, N. J. (1968). *J. Less-Common Metals*, **14**, 279.

STEEB, S. & GODEL, D. (1965). *Z. Metallk.* **56**, 612.

STEEB, S., GODEL, D. & LOHR, C. (1968). *J. Less-Common Metals*, **15**, 137.

VOGEL, R. E. & KEMPTER, C. P. (1961). *Acta Cryst.* **14**, 1130.

WANG, F. E. & GILFRICH, J. V. (1966). *Acta Cryst.* **21**, 476.

YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1960). *A Fortran IV Program for the Intensity Calculation of Powder Patterns*. Laboratory for Research on the Structure of Matter, Univ. of Pennsylvania, Philadelphia.