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# Crystal structure of $Ag_7Ca_2$ – a new intermetallic structure type ☆

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**Abstract**

Single crystals of $Ag_7Ca_2$ were grown and examined without the application of mechanical stress. The crystal structure was solved by single-crystal X-ray diffraction. $Ag_7Ca_2$ is orthorhombic, space group *Cmcm*, $a=9.478(2)$ Å, $b=5.525(1)$ Å, $c=14.079(2)$ Å, $Z=4$, $R=0.034$, with a simple new structure type containing Kagomé nets of silver atoms, surrounded by hexagonal and triangular nets of silver and calcium atoms. These layers are then stacked as in hexagonal close packing. Predicted mechanical properties are discussed briefly. The *c*-axis conductivity of $Ag_7Ca_2$, measured as a function of temperature on a single crystal, approaches that of silver metal.

*Keywords:* Crystal structure; X-ray diffraction; Silver; Calcium

## 1. Introduction

In a recent paper [1] we reported that the compound previously known [2] as $Ag_8Ca_3$ is actually a nitride with composition $Ag_{16}Ca_6N$. To verify this, we repeated the synthesis in the absence of nitrogen. We did not find any evidence of $Ag_8Ca_3$, but instead we were able to grow single crystals of $Ag_7Ca_2$, having a previously unknown intermetallic structure type. The structure is remarkably simple: slightly distorted hexagonal layers form close packed slabs which are stacked AB as in hexagonal close packing of spheres.

The alloys of silver and calcium have been studied extensively. Early powder X-ray diffraction work [3,4] indicated an intermetallic phase of nominal composition $Ag_3Ca$ with an f.c.t. cell. Thermodynamic investigations of the Ag–Ca phase diagram [5–7] have indicated the presence of phases with compositions $AgCa_3$, $Ag_3Ca_5$, AgCa, $Ag_2Ca$, $Ag_7Ca_2$, and $Ag_9Ca_2$. $Ag_7Ca_2$ melts congruently at 731 °C, as seen by a maximum in the liquidus curve at this composition. The compositions for $Ag_7Ca_2$ and $Ag_9Ca_2$ were apparently confirmed from the size of the unit cell in single-crystal X-ray diffraction examinations, and they replace the compositions $Ag_3Ca$ and $Ag_4Ca$ reported in previous literature. The reported diffraction pattern [3] of $Ag_3Ca$, however, does not conform to the structure of $Ag_7Ca_2$ reported here or to that of $Ag_{16}Ca_6N$.

Single-crystal structure analyses have been done for $Ag_3Ca_5$ [8], AgCa [9], and $Ag_2Ca$ [10] as well as '$Ag_8Ca_3$'. The approximate hexagonal cell for $Ag_7Ca_2$ ($a=5.50$ Å, $c=14.10$ Å, provisional space group $P6_322$) was mentioned by Villars and Calvert [11]. The compound $Ag_7Yb_2$ [12] is reported to have the same structure as $Ag_7Ca_2$.

## 2. Experimental

### 2.1. Synthesis following Refs. [1,2]

Distilled calcium metal (0.1297 g) and silver shot (0.9968 g) were melted together in a tantalum crucible at 750 °C under 1 atm purified argon. Cooling to 700 °C, the argon pressure was reduced to 15 mbar. After 5 days at 700 °C, some of the metal had transported above the main molten sample, forming needle-shaped crystals which grew radially inward from the walls of the tantalum crucible. These crystals were as long as several millimeters along [001], and were used for structure determination as well as conductivity exper-

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☆ Dedicated to the late Professor H.-U. Schuster.

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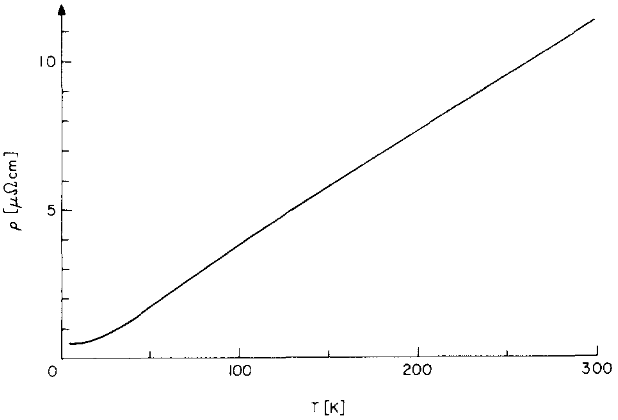

Fig. 1. c axis resistivity of $Ag_7Ca_2$.

iments. The remaining sample was very malleable and therefore complicated X-ray powder diffraction. The few reflections observed coincide with those of $Ag_7Ca_2$. An argon dry box was used when manipulating samples.

### 2.2. Electrical resistivity

The crystals of $Ag_7Ca_2$ are not noticeably reactive with the atmosphere over long periods (1 year), and therefore the sample for conductivity measurements was prepared in air. Silver epoxy paste was used for making contacts to a 1.5 mm × 0.025 mm × 0.025 mm needle at four positions along its length, with the voltage contacts 0.2 mm apart. Cooling and warming curves of the d.c. resistivity ($I = 10$ mA) are given in Fig. 1.

### 2.3. X-ray diffraction

22 reflections in the $\theta$ range 8.5°–29° were used for cell determination. The crystal structure was solved by direct methods and refined using SHELXL-93 and related software [13]. The absorption was calculated empirically using $\Psi$-scans with a laminar (100) model of the crystal shape with a 3° 'take off angle'. Additional correction for primary and secondary extinction was also necessary. Details of the single-crystal data collection are summarized in Table 1, the final atomic positional parameters, anisotropic thermal parameters and selected bond lengths are given in Tables 2, 3 and 4.

The orthorhombic unit cell constants for $Ag_7Ca_2$ differ by only 1.0% from an orthohexagonal cell ($b = a\sqrt{3}$). The structure does not refine using hexagonal space groups, and as discussed below contains an inherent asymmetry requiring an orthorhombic cell.

## 3. Results

### 3.1. Crystal chemistry

The molar volume of $Ag_7Ca_2$ is 89.2% that of the respective metals, which is consistent with the other three Ag–Ca phases whose crystal structures are known; they have molar volumes 89.0%–90.1% that of the pure metals.

The octahedral void produced by the close packing described below is slightly smaller than that required for a nitrogen or carbon atom. However, there is no crystallographic or chemical evidence for a non-metal atom at this site.

### 3.2. Description of structure

$Ag_7Ca_2$ contains two types of layer perpendicular to the c direction which are again only 1% off from having hexagonal symmetry. Two Ag(1) and four Ag(2) atoms lie in the same plane in a Kagomé net which forms an $Ag_6$ layer, with respect to the unit cell, shown in Fig. 2. Located above (and below) the triangles of the Kagomé net are the Ag(3) atoms which themselves form a hexagon net. Nearly coplanar with this net is a larger mesh triangular net of calcium atoms positioned directly above (and below) the center of each hexagon of the Kagomé net. These Ag(3) and calcium atoms together form a close-packed smaller mesh triangular layer, shown in Fig. 3, with stoichiometry of $Ag_4Ca_2$ per unit cell. The stacking of the layers is in general ...$[Ag_4Ca_2][Ag_6][Ca_2Ag_4]$..., where each $[Ag_4Ca_2][Ag_6][Ca_2Ag_4]$ slab has essentially close-packed atoms on both surfaces. The large calcium atoms in the $[Ag_4Ca_2]$ layers are depressed inward toward the $Ag_6$ layer providing a 'smoother' surface to the slabs.

Owing to the close-packed nature of the slab surfaces, adjacent slabs are quite naturally shifted 1.97 Å along $b$ (Fig. 4), to approximately the center of the triangular depression (1.83 Å away) in the neighboring slab. Alternating slabs have the same orientation, that is ABAB (hexagonal close packing) stacking sequence of triple layer $[Ag_4Ca_2][Ag_6][Ca_2Ag_4]$ slabs.

## 4. Discussion

In the notation of Pearson [14], the Kagomé net (6363) of the $Ag_6$ layer is represented by $\alpha$, the triangular net ($3^6$) of calcium by A, and the hexagon net ($6^3$) of Ag(3) by $a$. The $[Ag_4Ca_2][Ag_6][Ca_2Ag_4]$ slabs have $(a\underline{A})\alpha(\underline{A}a)$ (the calcium layers are underlined) stacking which is essentially the same coordination as that found in $CaCu_5$, $(a\underline{A})\alpha$. In $CaCu_5$ the $(a\underline{A})$ layers are coplanar. Indeed, $Ag_7Ca_2$ has a condensed $CaCu_5$ structure where every other $\alpha$ layer is removed. Other phases with the same stoichiometry, $Ce_2Ni_7$ and $Er_2Co_7$, develop a complicated layer pattern combining $CaCu_5$-type layers $(a\underline{A})\alpha$ with those of the Laves phase $MgZn_2$, $\alpha(\underline{A}B\underline{C})$, to make sequences of the type $\alpha(a\underline{A})\alpha(a\underline{A})\alpha(\underline{A}B\underline{C})$. The translation along $b$, of approximately one-third of the hexagonal base, is 90° from the typical translation

Table 1
Crystal data and structure refinement for $Ag_7Ca_2$

| | |
|---|---|
| Diffractometer type | Siemens R3m/V |
| Monochromator | Graphite |
| Empirical formula | $Ag_7Ca_2$ |
| Formula weight | 835.25 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | *Cmcm* (No. 63) |
| Unit cell dimensions | $a = 9.4784(18)$ Å, $\alpha = 90°$ |
| | $b = 5.5251(7)$ Å, $\beta = 90°$ |
| | $c = 14.0790(15)$ Å, $\gamma = 90°$ |
| Volume (Å$^3$) | 737.3(2) |
| $Z$ | 4 |
| Density (calculated) (g cm$^{-3}$) | 7.525 |
| Absorption coefficient (mm$^{-1}$) | 19.476 |
| $F(000)$ | 1476 |
| Crystal size (mm) | $0.04 \times 0.08 \times 0.36$ |
| $\theta$ range for data collection (deg) | 2.89–27.49 |
| Index ranges | $-12 \leq h \leq 12$, $0 \leq k \leq 7$, $0 \leq l \leq 18$ |
| Reflections collected | 815 |
| Independent reflections | 451 ($R_{\mathrm{int}} = 0.0325$) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data, restraints, parameters | 451, 0, 27 |
| Goodness-of-fit on $F^2$ | 1.062 |
| Final $R$ indices ($I > 2\sigma(I)$) | $R_1 = 0.032$, $w_{R2} = 0.079$ |
| $R$ indices (all data) | $R_1 = 0.034$, $w_{R2} = 0.081$ |
| Extinction coefficient | 0.069(3) |
| Largest diffraction peak and hole (eÅ$^{-3}$) | 2.323 and $-2.710$ |

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å$^2 \times 10^4$) for $Ag_7Ca_2$; $U$(eq) is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor

| Atom | Wyckoff position | $x$ | $y$ | $z$ | $U$(eq) |
|---|---|---|---|---|---|
| Ca | 8f | 0 | 0.3219(2) | 0.11471(12) | 130(4) |
| Ag(1) | 4c | 0 | 0.82668(11) | 1/4 | 108(4) |
| Ag(2) | 8g | 0.25088(5) | 0.07750(8) | 1/4 | 110(3) |
| Ag(3) | 16h | 0.33475(5) | 0.32926(7) | 0.07649(3) | 140(3) |

Table 3
Anisotropic displacement parameters [Å$^2 \times 10^4$] for $Ag_7Ca_2$; the anisotropic displacement factor exponent takes the form $-2\pi^2 [(ha^*)^2 U_{11} + \cdots + 2hka^*b^*U_{12}]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Ca | 129(9) | 120(8) | 142(9) | $-2(5)$ | 0 | 0 |
| Ag(1) | 64(5) | 109(5) | 151(5) | 0 | 0 | 0 |
| Ag(2) | 108(5) | 73(4) | 150(5) | 0 | 0 | $-27(2)$ |
| Ag(3) | 153(5) | 144(4) | 122(4) | 2(1) | $-4(1)$ | $-13(1)$ |

Table 4
Selected bond lengths (Å) for $Ag_7Ca_2$

| | | |
|---|---|---|
| Ca–Ca | ×1 | 3.782(3) |
| Ca–Ca | ×1 | 3.810(3) |
| Ca–Ag(1) | ×1 | 3.3337(14) |
| Ca–Ag(1) | ×1 | 3.378(2) |
| Ca–Ag(2) | ×2 | 3.3325(12) |
| Ca–Ag(2) | ×2 | 3.3465(12) |
| Ca–Ag(3) | ×2 | 3.1859(12) |
| Ca–Ag(3) | ×2 | 3.2184(8) |
| Ca–Ag(3) | ×2 | 3.224(2) |
| Ca–Ag(3) | ×2 | 3.2562(12) |
| Ag(1)–Ag(2) | ×2 | 2.7333(7) |
| Ag(1)–Ag(2) | ×2 | 2.7523(7) |
| Ag(1)–Ag(3) | ×4 | 2.9020(5) |
| Ag(2)–Ag(2) | ×2 | 2.7626(4) |
| Ag(2)–Ag(3) | ×2 | 2.9168(5) |
| Ag(2)–Ag(3) | ×2 | 2.9214(5) |
| Ag(3)–Ag(3) | ×1 | 2.8260(10) |
| Ag(3)–Ag(3) | ×1 | 2.8631(9) |
| Ag(3)–Ag(3) | ×1 | 3.1326(11) |
| Ag(3)–Ag(3) | ×2 | 3.1957(6) |

vector found in compounds with such layers, which we will denote as Z, $z$, and $\zeta$. The structure of $Ag_7Ca_2$ is then represented by $(a\underline{\mathrm{A}})\alpha(\underline{\mathrm{A}}a)(z\underline{\mathrm{Z}})\zeta(\underline{\mathrm{Z}}z)$.

It is the distinguishability of the calcium and silver atoms in the close packing layers that breaks the hexagonal symmetry when the layers are stacked ABAB (h.c.p.). It is impossible to stack (without having atoms eclipsed) a $6^3$ net on top of another which preserves the threefold symmetry; such a stacking is possible with Kagomé nets, as seen in $Ni_3Sn$. Thus each atom in a $[Ca_2Ag_4]$ layer with local $3m$ symmetry must coordinate to a triangle consisting of one calcium and two silver

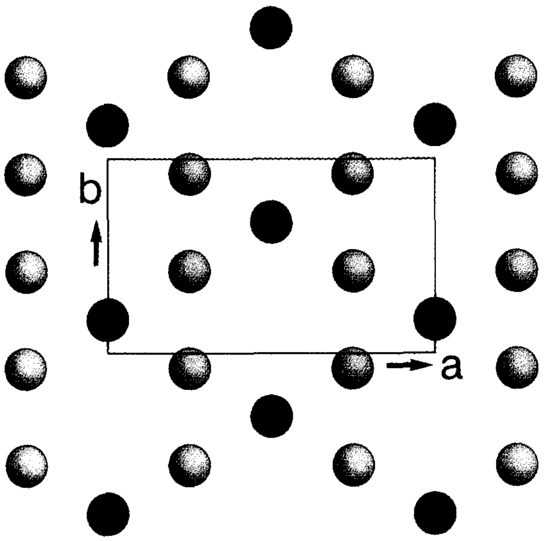

Fig. 2. Kagomé net of Ag(1) (lighter) and Ag(2) (darker) atoms, viewed along *c*. The unit cell is outlined in black.

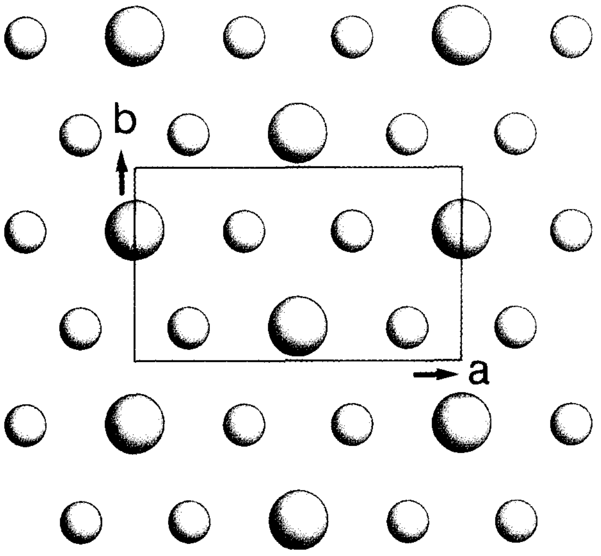

Fig. 3. $6^3$ net of Ag(3) atoms (small) and $3^6$ net of calcium atoms (large) making an [$Ag_4Ca_2$] layer, viewed along *c*. The unit cell is outlined in black.

atoms in the neighboring [$Ca_2Ag_4$] layer, reducing the maximum possible symmetry to *m*. The slight orthorhombic distortion produced by this arrangement must be sufficient to enforce further stacking of the slabs along *b*. There are nine equally accessible orientations for ($a\underline{A}$) nets, $Ag_7Ca_2$ uses only two. The h.c.p. type stacking allows orthorhombic symmetry while c.c.p. (ABC) stacking would reduce the cell symmetry further to monoclinic.

The calcium atoms in $Ag_7Ca_2$ have coordination number (CN) 16. This results from a hexagon of six Ag(3) atoms at an average distance of 3.22(3) Å within the [$Ca_2Ag_4$] layer, a hexagon of six Ag(1) and Ag(2) atoms at 3.35(2) Å in the adjacent $Ag_6$ layer, through the center of which is a calcium atom at 3.81 Å. On

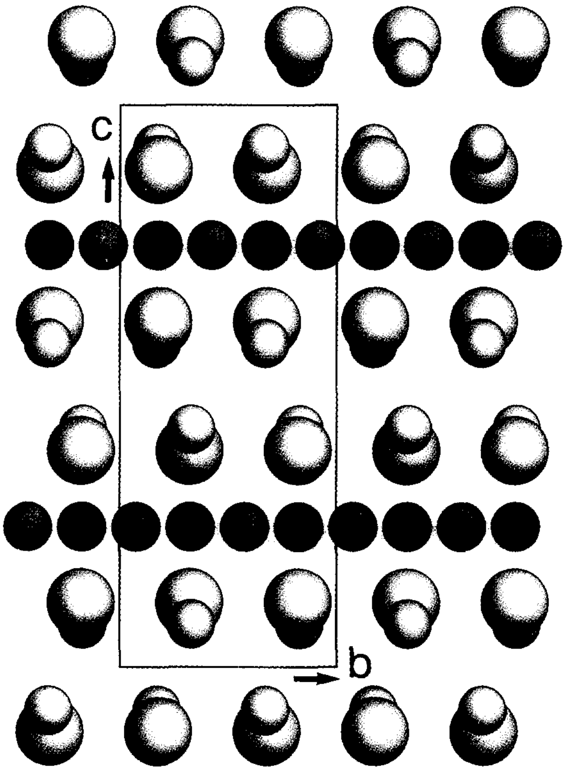

Fig. 4. Arrangement of [$Ag_4Ca_2$] layers (darker atoms) and $Ag_6$ layers (lighter atoms) as viewed along *a*. The unit cell, outlined in black, contains two [$Ag_4Ca_2$][$Ag_6$][$Ca_2Ag_4$] 'slabs', see text.

the opposite side is a triangle of two Ag(3) atoms at 3.225 Å and a calcium atom at 3.78 Å in the adjacent [$Ag_4Ca_2$] layer.

All the silver atoms have distorted cubo-octahedral coordination (CN = 12). The Ag(1) and Ag(2) atoms have essentially the same coordination sphere, four Ag(1) or Ag(2) atoms at 2.75(1) Å from within the $Ag_6$ layer, four Ag(3) at 2.91(1) Å and four calcium at 3.35(2) Å from the [$Ca_2Ag_4$] layers above and below. The Ag(3) atoms coordinate to three Ag(3) at 3.17(3) Å and three calcium at 3.23(3) Å from a hexagon within the [$Ca_2Ag_4$] layer, a triangle of two Ag(3) at 2.84(2) Å, one calcium at 3.22 Å from the neighboring [$Ca_2Ag_4$] layer, and a triangle of one Ag(1) and two Ag(2) at 2.91(1) Å from the other side. All of the atoms in $Ag_7Ca_2$ have interatomic distances comparable with those in other Ag–Ca intermetallics, as discussed previously in [1].

The other known structures in the Ag–Ca system have different layer structures and coordination than found in $Ag_7Ca_2$. AgCa has the BCr structure containing layers of $Cr_6B$ trigonal prisms. $Ag_3Ca_5$ has the $B_3Cr_5$ structure. $Ag_2Ca$ has the $Cu_2Ce$ structure type made of $3^25^2 + 3^45$ (2:1) nets.

The $Ag_{51}Gd_{14}$ structure type [15–17] contains similar ($3^6$) nets of gadolinium atoms coordinated to hexagon nets ($6^3$) of silver atoms. Unfortunately, the structure solution contains substantial disorder making it difficult to compare directly with $Ag_7Ca_2$.

From the simple layered structure of $Ag_7Ca_2$, it should be relatively easy for the close-packed slabs to slip in directions other than along *b*, namely directions at 60° from the *b* axis but still in the (001) plane. Such a crystal would give disordered atom positions. It is possible that the disordered nature of $Ag_{51}Gd_{14}$ and isostructural compounds results from such a slip mechanism. It is worth noting that the crystals reported in this work were used as grown and never exposed to any mechanical stress which is not usually the case for such compounds.

$Ag_7Ca_2$ is a very good metal as shown by the linear character of the *c* axis resistivity as a function of temperature, and the low room temperature resistivity of approximately $10^{-5}$ Ω cm compared with that of silver, $10^{-6}$ Ω cm.

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## References

[1] G.J. Snyder and A. Simon, *Angew. Chem., 106* (1994) 173; *Angew. Chem. Int. Ed. Engl., 33* (1994) 689.

[2] L.D. Calvert and C. Rand, *Acta Crystallogr., 17* (1964) 1175.

[3] C. Degard, *Z. Kristallogr., 90* (1935) 399.

[4] A. Iandelli, *Rend. Semin. Fac. Sci. Univ. Cagliari, 19* (1949) 133–139.

[5] N. Baar, *Z. Anorg. Allge. Chem., 70* (1911) 352.

[6] W.A. Alexander, L.D. Calvert, A. Desaulniers, H.S. Dunsmore and D.F. Sargent, *Can. J. Chem., 47* (1969) 611.

[7] M. Notin, *Calphad, 6* (1982) 49.

[8] R.P. Rand and L.D. Calvert, *Can. J. Chem., 40* (1962) 705.

[9] F. Merlo, *J. Less-Common Met., 86* (1982) 241.

[10] L.D. Calvert, H.S. Dunsmore, L.V. Kuhi and R.S. Tse, *Acta Crystallogr., 10* (1957) 775.

[11] P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases,* American Society for Metals, Metals Park, OH, 1985.

[12] Palen, *J. Less-Common Met., 21* (1970) 443.

[13] G.M. Sheldrick, Program for crystal structure refinement, *J. Appl. Crystallogr,.* in preparation.

[14] W.B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley-Interscience, London, 1972.

[15] A. Dommann and F. Hulliger, *J. Less-Common Met., 141* (1988) 273.

[16] D.M. Bailey and G.R. Kline, *Acta. Crystallogr. B, 27* (1971) 650.

[17] J.-P. Gabathuler, P. White and E. Parthé, *Acta Crystallogr. B, 31* (1975) 608.