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Note on the Structure of the Gamma Brass Like γ_3 Phase in the Silver Lithium System

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In a research project at this institute the structures of a number of gamma brass like phases have been studied. These phases generally form in systems between a transition metal (T or B^1) according to the nomenclature of Schubert¹) and a non-transition metal from the B^2 – B^4 groups of the periodic table. Several different ordering schemes have been observed for the metal atoms on the atomic sites of the general gamma structure type, which are,¹⁰ in space group $I43m$, those listed in Table I.

A definite tendency has been observed³ for the transition metal atoms to con-

centrate at the OT and OH sites in phases where the transition metal is taken from the T^9 , T^{10} , or B^1 group and the radius ratio $r(B)/r(T$ or $B^1)$ lies in the range 0.95–1.12.

No atomic ordering scheme has, so far, been definitely established for a gamma phase with a non-transition metal component outside the B^2 – B^4 range. In the Ag–Li system there occur three such phases,⁴ all of them cubic. Since silver is a B^1 metal and the radius ratio r_{Li}/r_{Ag} is 1.09, it was deemed to be of great interest to see whether or not the fact that the non-transition metal is in this case taken from another part of the periodic table would lead to the formation of a differently ordered structure.

Experimental. Preparations of the three phases, γ_1 , γ_2 , and γ_3 , homogeneous at room temperature in the approximate ranges⁴ 7–13, 16–23, and 26–36 atomic % Ag, respectively, were synthesized by fusion of the components in argon of atmospheric pressure. Weighed amounts of the materials (Ag, powder, Kebo 99.9 % and Li, granular, Merck, sodium content less than 0.05 %) were melted together in an iron crucible for approximately 15–30 sec, and allowed to cool without quenching. The loss of Li by evaporation was found to be very small, and the final compositions were taken to be equal to those calculated from the amounts of Ag and Li used. The γ_1 and γ_2 preparations were quite sensitive to atmospheric corrosion and were, moreover, soft so that the pellets could not be easily crushed. Thus, the γ_3 -containing charges which were more stable in air, and easier to prepare powder specimens from, were the only ones used for the continued investigation.

X-Ray powder photographs for the determination of lattice parameters were taken in a focusing Guinier-Hägg camera of 80 mm diameter, with strictly monochromatized $CuK\alpha_1$ radiation ($\lambda=1.54050$ Å), and with KCl ($a=6.2919$ Å⁵) as an internal standard.

The diffracted intensities were more accurately determined by means of a powder diffractometer¹¹ employing crystal monochromatized $CuK\alpha$ radiation.

For the calculation of theoretical powder intensities from tentative structure models, Lp-factors were computed according to Sagel,⁶ and the atomic scattering factors and dispersion corrections given by Cromer and Waber,⁸ and Cromer,⁹ respectively, were used.

Results. A preparation which proved to contain γ_3 phase, with only very small

Table 1. Structural parameters for the γ_3 -Ag,Li phase.

Weighed-in composition	$\text{Ag}_{0.302} \text{Li}_{0.698}$
Assumed composition of model	$\text{Ag}_{0.308} \text{Li}_{0.692} = \text{Ag}_4 \text{Li}_9$
Lattice parameter	$a = 9.6018 \pm 8 \text{ \AA}$
Measured density	$d_o = 3.62 \text{ g cm}^{-3}$
Calculated density	$d_c = 3.70 \text{ g cm}^{-3}$
Unit cell content	$Z = 52 \text{ atoms}$
Space group	$I43m \text{ (No. 217)}$
Atomic position and occupancy parameters	
IT (8 Li)	8(c) $x, x, x; x = 0.10$
OT(6.4 Ag+ 1.6 Li)	8(c) $x, x, x; x = -0.17$
OH(9.6 Ag+ 2.4 Li)	12(c) $x, 0, 0; x = 0.35$
CO(24 Li)	24(g) $x, x, z; x = 0.30$ $z = 0.05$

amounts of other phases present, had the composition, density, assumed space group and lattice parameter of the b.c.c. unit cell listed in Table 1.

The atomic position parameters, given in the same table, were assumed to be approximately the same as in, *e.g.*, Cu_5Zn_8 or $\text{Ni}_5\text{Zn}_{11}$,⁷ with size factors 1.07 and 1.10, respectively; and with the same, body-centered, symmetry.

The lowest $R_I = 100 \times \sum |I_o| - |I_c| / \sum |I_o| = 10\%$ was observed for the atomic ordering recorderd in Table 1, implying a completely disordered distribution of 16 silver atoms over the 20 sites of the OT and OH positions.

Models with the same amount of silver differently distributed over these two positions gave higher R_I values, ranging up to 17%; a distribution with the OT position completely occupied by Ag and the OH position containing 67% Ag, 33% Li yielded $R_I = 13\%$. All other distributions tried yielded much higher values: $R_I = 32-109\%$. Inspection of the correspondence between I_o and I_c for the low-angle reflections (notably for $\sum h^2 = 4$) also proved these further models to be seriously in error.

In Table 2 are given I_o and I_c for the best structure model obtainable with the synthetic composition given. It may be noted that the calculated intensities of a few unobserved high-angle lines are higher than some actually observed low-angle intensities. The high-angle reflections were generally diffuse, however, and thus not so easily observed. Consequently, observed intensities were only recorded for $\sum h^2 \leq 66$.

The positions at which the Ag atoms enter in the structure are the expected

Table 2. Intensities for the γ_3 -Ag,Li model. $R_I = 10\%$. I_o recorded for $\sum h^2 \leq 66$.

$\sum h^2$	I_o	I_c	$\sum h^2$	I_c
2	268	373	68	189
4	160	276	70	35
6	8434	9352	72	634
8	647	621	74	188
10	—	192	76	6
12	602	656	78	372
14	463	344	80	38
16	—	19	82	29
18	10590	10760	84	197
20	—	36	86	97
22	—	106	88	0
24	1406	1325	90	1334
26	—	128	94	5
30	995	599	96	141
32	—	1	98	393
34	—	46	100	28
36	2198	1272	102	555
38	—	352	104	166
40	—	21	106	10
42	858	858	108	471
44	—	52	110	71
46	—	20	114	781
48	—	327	116	78
50	—	224	118	8
52	—	5	120	618
54	2939	2908	122	285
56	—	6		
58	—	9		
62	—	86		
64	—	9		
66	1044	1264		

ones, but the distribution over these sites differs somewhat from what has been observed for the "normal" gamma phases.⁸ In these, the OT position is first completely

filled with transition metal atoms, and the rest of these atoms statistically distributed over the OH position.

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