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The crystal structure of the $LiAg_2In$ compound

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Abstract

The newly established intermetallic compound $LiAg_2In$ crystallizes in the $MnCu_2Al$-type structure (Fm-3m, Heusler phase) with $a = 6.5681(5)$ Å. The homogeneity range of this phase in the ternary Li–Ag–In phase diagram along the adjacent quasibinary cut $Li_{0.25}(Ag_{1-x}In_x)_{0.75}$ was determined by X-ray powder diffraction and extends from $x\sim0.33$, $Li_{0.25}Ag_{0.50}In_{0.25}$, up to $x\sim0.44$, $Li_{0.25}Ag_{0.42}In_{0.33}$. The homogeneity ranges of Heusler- and Zintl-type phases in the Li–Ag–In system are separated from each other by a broad heterogeneous region.

Keywords: Zintl phase; Heusler phase; $LiAg_2In$; $Li_{0.25}(Ag_{1-x}In_x)_{0.75}$

1. Introduction

Binary and ternary lithium alloys have intensively been studied, and more than 130 ternary lithium compounds with Li_2TX or LiT_2X (T: d-metals; X: p-elements) composition are already known [1–4]. Many of these compounds crystallize in faced-centred cubic structures with 16 atoms in the unit cell, where each atom is hexaedrically surrounded by eight atoms in the nearest-neighbour shell. These structures are derived either from the NaTl-type structure (then called Zintl phases) or from the CsCl-type structure (then called Heusler phases). The striking difference between both structure types is the element distribution in the nearest-neighbour shell: The atoms with 50% share in the formulae, i.e. Li in Li_2TX or T in LiT_2X, are surrounded by four like- and four unlike atoms in the Zintl phases, but by eight unlike atoms in the Heusler phases as CsCl-type superstructure. Examples for these Li-containg Heusler phases are $LiAg_2Ge$ [5] and $LiAg_2Sn$ [6], for Li-free ones $MnCu_2Al$ [7] (space group Fm-3m).

In Zintl phases the two atom types with 25% share in the formulae, i.e. T and X in Li_2TX or Li and X in LiT_2X, can either be fully ordered on distinct sites, then called ordered Zintl phases or XA-structures (space group F-43m) [1,2], or are distributed with mixed occupancies, then called statistical Zintl phases or B32A-structures (space group Fd-3m) [1,2]. Statistical Zintl phases are only observed for very similar atomic radii of the atoms with 50% share in the formulae, on one hand, and the average of the radii of the two atom types with 25% share in the formula, on the other. The ordered Zintl phases tolerate also less hard radii restrictions. Examples for statistical Zintl phases are Li_2AgTl and Li_2AgIn [1,2], the latter in case of some Li-excess, i.e. for a Li-content $\geqslant 50\%$. Ordered Zintl phases are Li_2AuSn, Li_2AuIn [1,2], and Li_2AgIn in case of some Li-deficiency, i.e. for a Li-content $< 50\%$ [8]—an example for Li-free compounds with this structure is Hg_2CuTi [9]. In the frame of a comprehensive study of the Li–Ag–In phase diagram the homogeneity range of the Li_2AgIn Zintl phase [1,2] was completed recently [8], but the crystal structure of $LiAg_2In$ has not been reported yet. In this work we report on the crystal structure determination for $LiAg_2In$ by single-crystal X-ray diffraction and the investigation of the

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corresponding homogeneity range along the quasibinary cut $Li_{0.25}(Ag_{1-x}In_x)_{0.75}$ by X-ray powder diffraction.

2. Sample preparation

The investigated samples were prepared from the following reactants: lithium (rod of 10 mm diameter, 99.9 at%), indium (ingots, 99.999 at%) and silver (wire 99.999 at%). Appropriate amounts were mixed according to the aimed stoichiometry of the product and filled into unalloyed iron crucibles in the glove box under argon atmosphere. These crucibles have been sealed by welding under dry argon atmosphere, placed into a preheated furnace (1100 °C), and heavily shaked to mix up the molten reactants properly. After 10 min, the samples were rapidly cooled down to room temperature by removing the crucibles from the furnace into ambient conditions.

The amount of Li loss during sample preparation in hermetically closed crucibles can be estimated, based on previous studies with successive detailed chemical analyses of similar systems [1,10–12]. Accordingly, an alkaline loss up to 1 at% in nominal composition can be expected [8].

3. Structure determination of $LiAg_2In$

Suited gold-coloured single crystals were screened using a light microscope with the sample under dried paraffin as protection measure against humidity and used for single-crystal X-ray diffraction. Intensity data were collected in 7 φ-scans using the Xcalibur diffractometer from Oxford Diffraction, equipped with the Sapphire2 CCD detector and the ENHANCE X-ray source option. All observed reflections can be indexed, based on a face-centred cubic cell, $a = 6.5681(5)$ Å, without any additional extinction rules. A combined empirical absorption correction with frame scaling was applied, using the *SCALE3 ABSPACK* command in CrysalisRed [13]. The structure has been solved by direct methods and refined using the SHELX-97 package program [14]. An initial parameter set was obtained from automatic interpretations of direct methods using SHELXS-97, and this structure model was further refined until convergence using SHELXL-97. The calculated intensities are very similar for both a Zintl- and a Heusler-type structure model, because the differences are only due to different Ag and In distributions and the scattering power of Ag and In is very similar for X-rays. Therefore, both models have been used for structure refinements. In both cases the minimum R_1 values are obtained for a slight Li-deficiency δ, i.e. with some In/Ag on the Li site. (Most probably the Li-deficiency on its site is not to be assigned to a respective bulk composition loss but rather to a respective vice versa replacement of the heavy atoms on their sites by some Li atoms.) The final R_1 values are compared for both structure models as a function of Li-deficiency in Fig. 1. A Heusler-type structure model with $\delta \sim 0.06$ is clearly preferred against a Zintl-type model, in spite of the only small differences between Ag and In for X-rays. The final parameters for the model with the lowest R_1 value are summarized in Table 1, atomic coordinates and equivalent isotropic displacement parameters in Table 2. The unit cell and the coordination polyhedra are shown in Fig. 2.

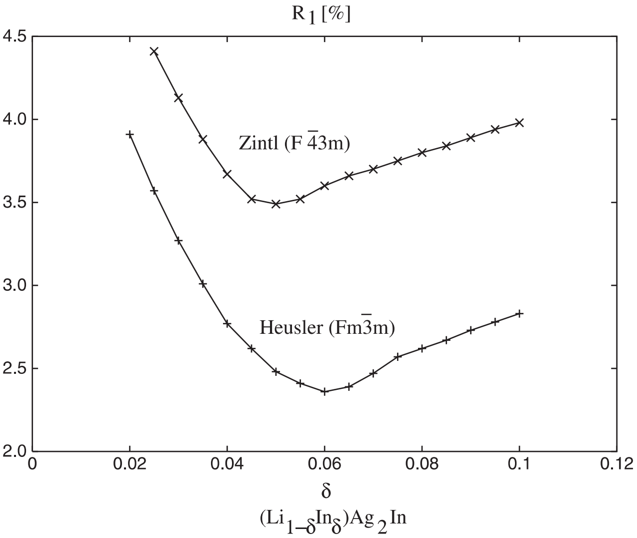

Fig. 1. Comparison of R_1 values for different degrees δ of In/Ag-occupation on the Li site for both structure models, Zintl and Heusler types.

Table 1
Crystal data and structure refinement for $LiAg_2In$

Empirical formula	$(Li_{0.94}In_{0.06})Ag_2In$
Formula weight	337.50
Temperature	298(2) K
Wavelength	0.071073 nm
Crystal system, space group	Cubic, *Fm-3m* (225)
Unit cell dimensions	$a = 6.5681(5)$ Å
Volume	283.35(4) Å^3
Z, Calculated density	4, 7.912 g/cm^3
Absorption coefficient	21.85 mm^{-1}
$F(000)$	595
Theta range for data collection	5.38–31.07°
Index ranges	$-9 \leqslant h \leqslant 9$, $-9 \leqslant k \leqslant 9$, $-8 \leqslant l \leqslant 8$
Reflections collected/unique	480/39 [$R_{(int)} = 0.0892$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	39/0/5
Goodness-of-fit on F^2	1.460
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0235$, w$R_2 = 0.0824$
R indices (all data)	$R_1 = 0.0235$, w$R_2 = 0.0824$
Extinction coefficient	0.003(1)
Largest diff. peak and hole	1.06 and −0.89 e A^{-3}

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $LiAg_2In$

Atom	Site	x/a	y/b	z/c	U
4 In	4*a*	0	0	0	0.021 (1)
8 Ag	8*c*	1/4	1/4	1/4	0.024 (1)
3.76Li + 0.24In	4*b*	1/2	1/2	1/2	< 0.003

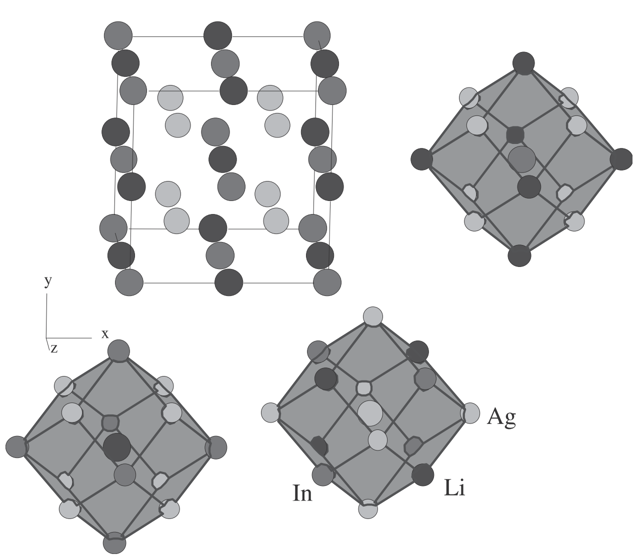

Fig. 2. Unit cell and coordination polyhedra of the atoms in the structure of the $LiAg_2In$ compound.

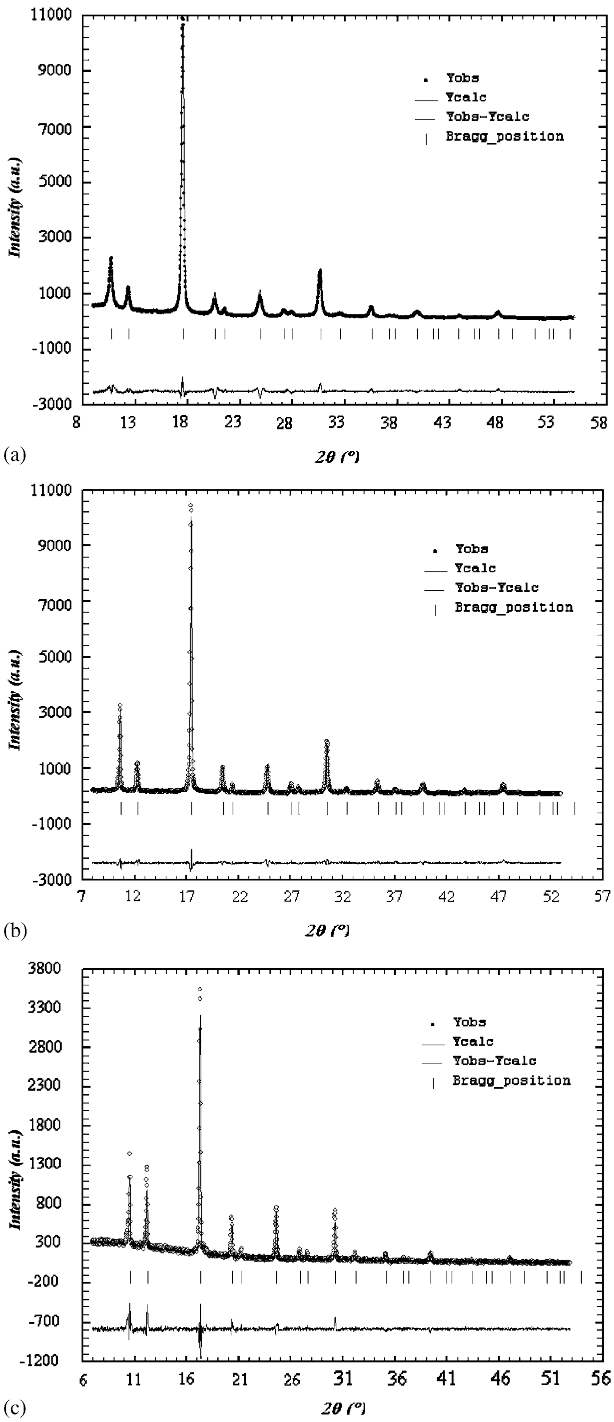

Fig. 3. Observed and calculated X-ray powder diffraction patterns together with their difference curve for $Li_{25}Ag_{50}In_{25}$ (a), $Li_{24.8}Ag_{46.5}In_{28.7}$ (b), $Li_{25}Ag_{42}In_{33}$ (c) alloys. Note that intensities are affected by non-ideal powder statistics due to coarse grain sizes.

4. Powder patterns of the quasibinary cut $Li_{0.25}(Ag_{1-x}In_x)_{0.75}$ (including $LiAg_2In$)

X-ray powder diffraction patterns were collected on a STOE STADI P (Mo*K*α_1 radiation) in Debye–Scherrer mode. In a glove box filled with argon, the very hard samples were ground in an agate mortar or filed, filled in capillaries of 0.3 mm diameter and sealed. Capillaries “no. 14” from Hilgenberg (Germany) were chosen because of less electrostatic adhesion than for capillaries “no. 50”. Intensities were recorded for diffraction angles 2θ from 7° to 58° in steps of $\Delta 2\theta = 0.02°$, using a linear position sensitive detector with 6° aperture. The software package WinPlotr was used for Rietveld refinements [15].

The X-ray powder pattern of the alloy with the nominal composition $LiAg_2In$ after remelting and slow cooling to room temperature in 20 h revealed only reflections from the Heusler phase (or of the ordered Zintl phase—the calculated powder diffraction intensities are too similar to distinguish both models by X-ray powder diffraction). No additional phase was observed. The experimental X-ray diffraction pattern, calculated profiles and their difference curve after Rietveld refinement are shown in Fig. 3. The results, see Table 3, also confirm agreement between powder data and the model from the single crystal study, based on the $MnCu_2Al$-structure type (Heusler phase). For the investigation of the homogeneity range of this

Table 3
Rietveld refinement for the samples from the homogeneity range of the Heusler-type phase along the quasibinary cut $Li_{0.25}(Ag_{1-x}In_x)_{0.75}$

Composition				$Li_{25}Ag_{50}In_{25}$		$Li_{24.8}Ag_{46.5}In_{28.7}$		$Li_{25}Ag_{42}In_{33}$	
Structure type						$MnCu_2Al$			
Space group, Pearson symbol, *Z*						*Fm*-3*m*, *cF*16, $Z = 4$			
Lattice parameters				$a = 6.5696(3)$ Å		$a = 6.5989(2)$ Å		$a = 6.6427(3)$ Å	
Number of reflections used in refinement				31		29		29	
2θ range				$9.00 < 2\theta < 57.99$		$8.00 < 2\theta < 52.98$		$7.00 < 2\theta < 52.88$	
No. of fitted parameters				21		22		32	
R_p, R_{wp}, R_B, R_F				6.43, 8.77, 4.72, 16.0		6.48, 8.35, 4.16, 5.18		9.06, 11.9, 11.2, 8.17	
Site	*x*/*a*	*y*/*b*	*z*/*c*	Atom	$B \times 10^{-2}\,nm^2$	Atom	$B \times 10^{-2}\,nm^2$	Atom	$B \times 10^{-2}\,nm^2$
4(*a*)	0	0	0	4 In	2.92 (5)	4In	2.92 (2)	4 In	2.78 (2)
4(*b*)	1/2	1/2	1/2	M1	3.20 (6)	M1	3.20 (2)	M1	4.75 (2)
8(*c*)	1/4	1/4	1/4	M2	2.45 (4)	M2	2.45 (4)	M2	3.72 (4)
M1				3.62 Li + 0.38 In		3.78 Li + 0.22 In		4 Li	
M2				8 Ag		7.44 Ag + 0.56 In		6.72 Ag + 1.28 In	

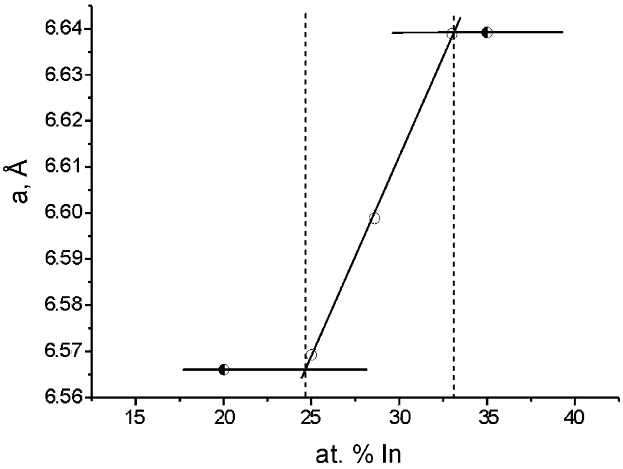

Fig. 4. Change of the lattice parameters in the homogeneity range of the $Li_{0.25}(Ag_{1-x}In_x)_{0.75}$ Heusler phase (○—single-phase alloy, ◐—two-phase alloy).

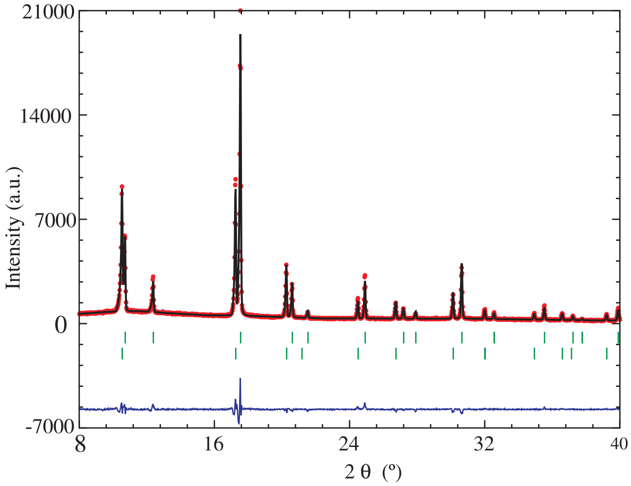

Fig. 5. Observed and calculated diffraction patterns of $Li_{0.38}Ag_{0.31}In_{0.31}$, based on the proposed model of two coexisting phases (Heusler and Zintl phases with upper and lower lines of reflection marks, respectively, heterogeneous region). The difference curve is also shown.

phase at 25% Li-content 6 alloys with next compositions $Li_{25}Ag_{55}In_{20}$, $Li_{25}Ag_{50}In_{25}$, $Li_{24.8}Ag_{46.5}In_{27.8}$, $Li_{25}Ag_{42}In_{33}$, $Li_{25}Ag_{40}In_{35}$, and $Li_{25}Ag_{35}In_{40}$ were prepared. The samples with composition $Li_{25}Ag_{50}In_{25}$, $Li_{24.8}Ag_{46.5}In_{28.7}$, $Li_{25}Ag_{42}In_{33}$ are single-phase alloys, and their crystal structures were refined by Rietveld method. Most probably in these Heusler-phase alloys a successive displacement of the Ag atoms by the In atoms takes place on the (8*c*) site. The change of the lattice parameters in the homogeneity range of this quasibinary cut is in good agreement with Vegard's law as shown in Fig. 4. As the used powders were relatively coarse grained the experimental intensities deviate from the calculated ones sometimes more than expected from counting statistics (especially obvious for the $Li_{25}Ag_{42}In_{33}$ alloy); nevertheless, the homogeneity region along this quasibinary cut can still be fixed reliably.

5. Two-phase region between the Heusler and the Zintl phase

The broad homogeneity range of a Zintl phase around Li_2AgIn has already been described in [1,2,8]. This region is separated from the here-described Heusler phase around $LiAg_2In$ by a broad heterogeneous two-phase region of both phases, deduced from the investigtion of five alloys with different compositions. The coexistence of two phases is most clearly demonstrated for the averaged composition $Li_{0.38}Ag_{0.31}In_{0.31}$, see Fig. 5, where both phases have nearly the same share.

6. Conclusion

The alloy $LiAg_2In$ crystallizes in a (ordered) Heusler structure, i.e. in the space group *Fm*-3*m*. The atoms occupy the Wyckoff point positions as follows: In on (4*a*), Li on (4*b*), Ag on (8*c*), i.e. the Ag atoms are hexaedrically surrounded by eight unlike atoms (four In and four Li atoms) in the nearest-neighbour shell. A slight occupation of the Li site by about 6% with In or Ag is observed, most probably compensated by a respective vice versa occupation of the In and/or Ag sites by 6% of Li.

The preference of this structure versus the ordered Zintl phase structure for this compound is additionally confirmed by the earlier finding that the broad homogeneity range of the Zintl phase in the Li–Ag–In phase diagram, adjacent to the binary LiIn system, is separated from the here-discussed homogeneity range of the Heusler phase, adjacent to the $LiAg_2In$ compound, by a heterogeneous two-phase region [8].

In the $LiAg_2In$-including homogeneity range of the quasibinary cut $Li_{0.25}(Ag_{1-x}In_x)_{0.75}$ with $0.33 \leqslant x \leqslant 0.44$ the Ag atoms on the (8*c*) positions are successively replaced by the In atoms, most probably under preservation of the Heusler structure.

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