

Two cubic polymorphs of AlGeLi

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Received 9 February 2005

Accepted 7 March 2005

Online 30 April 2005

Aluminium germanium lithium, AlGeLi, crystallizes in two cubic dimorphs. The structure of the $F\bar{4}3m$ form, already inferred from powder data, has been confirmed by both powder and single-crystal X-ray diffraction studies. The second dimorph, not previously identified, adopts a disordered centrosymmetric structure with space group $Fm\bar{3}m$.

Comment

So far, the literature related to the ternary system Li–Al–Ge has been very poor. On the basis of X-ray powder diffraction, a cubic non-centrosymmetric structure has been proposed for AlGeLi, with either ordered or disordered atomic arrangements (Nowotny & Holub, 1960; Bockelman & Schuster, 1974; Schuster *et al.*, 1976). In all cases, the structure was depicted with one among four $\bar{4}3m$ sites empty. Bockelman & Schuster (1974) refer to the cubic compound AlGeLi₂ ($a = 6.163 \text{ \AA}$) without giving any more structural details. We decided to synthesize the compounds AlGeLi and AlGeLi₂ in order to define precisely their crystal structures.

The alloy prepared with a 1:1:1 stoichiometry leads to a homogeneous product, for which the X-ray powder diffraction

pattern was perfectly indexed in a cubic cell [$a = 5.9913 (1) \text{ \AA}$] and further refined by the Rietveld technique in space group $F\bar{4}3m$ to good agreement factors ($R_p = 7.66\%$ and $R_{\text{Bragg}} = 4.92\%$). Meanwhile, the structure and the absolute configuration [Flack (1983) parameter = $-0.02 (4)$] were determined from good quality intensity data ($R_{\text{int}} = 4.00\%$) collected from a single crystal [$a = 5.9784 (9) \text{ \AA}$] on a Nonius single-point detector diffractometer. The structure refinement was carried out to an $R(F)$ value of 1.11% [inversion of the configuration leads to an $R(F)$ value of 5.85%]. Our results confirm the ordered and non-centrosymmetric atomic arrangement for the AlGeLi polymorph I (Fig. 1 and Table 1). The atomic arrangement along the body diagonal of the cubic cell is vacancy (0, 0, 0) – Al ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) – Ge ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) – Li ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$).

All attempts to prepare AlGeLi₂ were unsuccessful. Starting from a 1:1:2 stoichiometry, we obtained a material that displayed a two-phase X-ray powder pattern, with the main component indexed in a cubic cell with an a parameter of 6.1528 (2) \AA . The minor component lines were indexed using the *DICVOL* program (Boultif & Louer, 1991) in an I -centered tetragonal cell ($a = 3.842 \text{ \AA}$ and $c = 8.544 \text{ \AA}$). A single crystal was extracted from this mixture and diffraction intensities were recorded. The statistical tests from *SHELXS97* (Sheldrick, 1997) gave strong evidence for centrosymmetry. The structure was first solved and refined with a disordered atomic arrangement in the space group $Fm\bar{3}m$ [$a = 6.1370 (8) \text{ \AA}$ and $R(F) = 3.76\%$].

Attempts to refine the structure in the other cubic symmetries $F\bar{4}3m$, $F432$ ($m\bar{3}m$ Laue symmetry), $Fm\bar{3}$ and $F23$ ($m\bar{3}$ Laue symmetry) gave no improvement. Since in some cases twinning can simulate centrosymmetry, we submitted the data to the twinning test server (Yeates, 1997); there was no hint of merohedral (perfect or partial) twinning. Nevertheless, we have tested various combinations of merohedral (mirror plane or twofold axis) and inversion twinning without success. Finally, the best solution was obtained in the $Fm\bar{3}m$ centrosymmetric space group with Li/Al atomic mixing at site $4b$. The refinement of AlGeLi polymorph II (Fig. 2 and Table 2) is in accordance with the Al/Ge and Al/Li ratios obtained from SEM–EDX (scanning electron microscopy/energy-dispersive X-ray diffraction) and atomic absorption (AA) analyses.

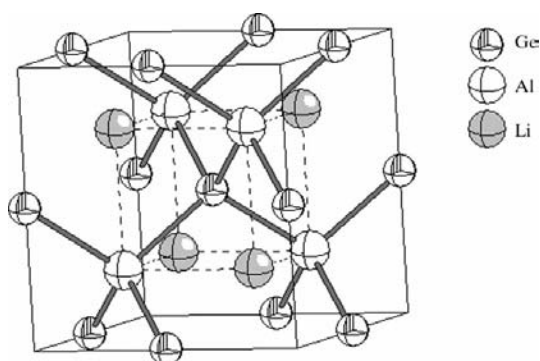


Figure 1
Representation of the cubic cell of the $F\bar{4}3m$ AlGeLi polymorph I.

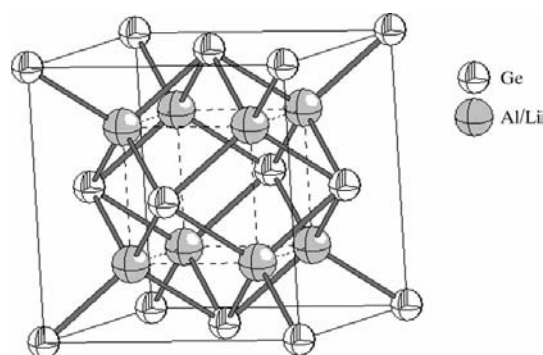


Figure 2
Representation of the cubic cell of the $Fm\bar{3}m$ AlGeLi polymorph II.

In the non-centrosymmetric ordered form I, the Ge atom is tetrahedrally surrounded by four Al and four Li atoms at 2.5886 (4) Å. In centrosymmetric disordered polymorph II, four Al and four Li atoms are statistically arranged at 2.6574 (4) Å at the apices of a cube around the Ge atom. Such statistical disorder in the Ge neighborhood might be responsible for the expansion of the unit cell.

In order to quantify how much such disorder can modify the unit-cell parameters, we have performed plane-wave DFT (density functional theory) calculations in the GGA/PBE approximation using the program *CASTEP* (Payne *et al.*, 1992) distributed as part of *MaterialsStudio* (Accelrys, 2002). Ultrasoft pseudopotentials were used for all atoms. The atomic disorder in polymorph II was modeled with the $2 \times 2 \times 2$ supercell that retains the $Fm\bar{3}m$ symmetry. Geometry was optimized in the supercell with Ge atoms at sites *a* (multiplicity 4), *b* (4) and *d* (24), and Li and Al atoms at *f* (32) (*x, x, x*, with refined *x* = 0.6233 and 0.8705, respectively). The optimized unit-cell parameter of 6.0921 Å for the subcell only deviates by 0.73% from the experimental value (*a* = 6.1370 Å). By comparison, geometry optimization of the $F\bar{4}3m$ unit cell of polymorph I gave 6.0264 Å instead of 5.9784 Å (experimental, 0.80% deviation). The calculated total energies indicate that the non-centrosymmetric polymorph I is more stable than the centrosymmetric polymorph II. The hypothetical compound AlGeLi₂ obtained by the Li-filling of vacancies in the cubic AlGeLi structures would display a cell parameter of 6.252 ($Fm\bar{3}m$) or 6.406 Å ($F\bar{4}3m$) (Tillard *et al.*, 2005).

In conclusion, we can assert that the compound AlGeLi exists in two cubic forms. The Al/Li substitutional disorder at site 4*a* ($Fm\bar{3}m$ centrosymmetric structure) is responsible for the 0.16 Å increase in the *a* cell parameter with respect to the ordered $F\bar{4}3m$ structure.

Experimental

Germanium powder (Strem Chemicals, 99.999% pure) was used without purification, and aluminium foil (Goodfellow, 99.999% pure, 0.5 mm) and lithium (ingot, Gogema, 99.94% pure, Mg free) were scraped to remove surface impurities. Alloys were prepared from the elements inside tantalum tubes, weld-sealed under an argon atmosphere, and enclosed in stainless steel or silica jackets filled with argon to protect tantalum from oxidation at high temperatures. Mixtures of elements were heated to an appropriate temperature (~1273 K) and kept at this temperature for several hours, during which period they were shaken several times to ensure good homogenization of the melts. The mixtures were then allowed to cool slowly to room temperature for crystal growth. Alloys were prepared at atomic ratios of 1:1:1 and 1:1:2 with the aim of obtaining the compounds AlGeLi and AlGeLi₂ previously cited in the literature. Crystals resulting from the two preparations were selected using a microscope inside a glove-box filled with purified argon. These crystals were inserted into thin-walled glass capillaries and then sealed to be used for checking singularity and crystal quality and for further X-ray investigations. The best diffracting single crystals were chosen for data collection at room temperature.

Polymorph I

Crystal data

AlGeLi
M_r = 106.51
 Cubic, $F\bar{4}3m$
a = 5.9784 (9) Å
V = 213.67 (6) Å³
Z = 4
D_x = 3.312 Mg m⁻³
 Mo *K*α radiation

Cell parameters from 25 reflections
 θ = 5.9–20.9°
 μ = 14.25 mm⁻¹
T = 293 (2) K
 Platelet, metallic dark grey
 0.12 × 0.07 × 0.03 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω/θ scans
 Absorption correction: numerical (*SHELXL76*; Sheldrick, 1976)
T_{min} = 0.32, *T_{max}* = 0.68
 1083 measured reflections
 67 independent reflections
 67 reflections with *I* > 2σ(*I*)

R_{int} = 0.040
 θ_{\max} = 34.5°
h = 0 → 9
k = 0 → 9
l = -9 → 9
 3 standard reflections every 100 reflections
 intensity decay: <1%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.011
wR(*F*²) = 0.028
S = 1.27
 67 reflections
 6 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0094P)^2 + 0.1227P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.030 (4)
 Absolute structure: Flack (1983), 28 Friedel pairs
 Flack parameter: -0.02 (4)

Table 1

Selected interatomic distances (Å) for (I).

Ge–Al ^I	2.5886 (4)	Li–Al	2.9890 (5)
Ge–Li	2.5886 (4)		

Symmetry code: (i) *x, y* - ½, *z* - ½.

Polymorph II

Crystal data

AlGeLi
M_r = 106.51
 Cubic, $Fm\bar{3}m$
a = 6.1370 (8) Å
V = 231.14 (5) Å³
Z = 4
D_x = 3.061 Mg m⁻³
 Mo *K*α radiation

Cell parameters from 1298 reflections
 θ = 5.8–34.6°
 μ = 13.17 mm⁻¹
T = 293 (2) K
 Triangle, metallic dark grey
 0.15 × 0.12 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
 ω scans
 Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2001; Clark & Reid, 1995)
T_{min} = 0.20, *T_{max}* = 0.41
 1298 measured reflections

41 independent reflections
 41 reflections with *I* > 2σ(*I*)
R_{int} = 0.071
 θ_{\max} = 34.6°
h = -9 → 9
k = -9 → 9
l = -9 → 9

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.038
wR(*F*²) = 0.090
S = 1.27
 41 reflections
 4 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 2.038P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.93 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.72 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.07 (2)

Table 2

Selected interatomic distances (Å) for (II).

Ge—Li1/Al1	2.6574 (4)	Li1/Al1—Li1/Al1	3.0685 (5)
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For compound (I), data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: local program. For compound (II), data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*. For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1121). Services for accessing these data are described at the back of the journal.

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