Crystal structure of aluminum germanium manganese (72.0:26.3:57.7), $\text{Al}_{72.0}\text{Ge}_{26.3}\text{Mn}_{57.7}$

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Abstract

$\text{Al}_{72.0}\text{Ge}_{26.3}\text{Mn}_{57.7}$, orthorhombic, *Pnma* (no. 62), $a = 14.516(2) \text{ \AA}$, $b = 12.484(2) \text{ \AA}$, $c = 12.405(2) \text{ \AA}$, $V = 2248.0 \text{ \AA}^3$, $Z = 1$, $R_{\text{gt}}(F) = 0.036$, $wR_{\text{ref}}(F^2) = 0.108$, $T = 297 \text{ K}$.

Source of material

A needle-like crystal was picked up from a master ingot with nominal composition of $\text{Al}_{40}\text{Mn}_{35}\text{Ge}_{25}$, which was prepared by arc-melting the mixture of pure Al, Mn and Ge in an argon atmosphere. The chemical composition of the title compound $\text{Al}_{46.1}\text{Mn}_{37.0}\text{Ge}_{16.9}$ was determined by the electron probe micro-analysis. Another crystalline phase, $\text{Al}_{34.5}\text{Mn}_{33.7}\text{Ge}_{31.8}$, which is frequently discussed as a magnetic ternary AlMnGe alloy [1], was also appeared in the present sample.

Discussion

Since the discovery of quasicrystals in rapidly solidified Al-rich manganese alloys [1,2], the so-called approximant structures have been used for providing structural models of quasicrystals. In particular, the crystal structure of Al_3Mn with a pentagonal columnar structure serves an essential idea for the structure of decagonal quasicrystal with a period of about $12 \text{ \AA}$ [3–6]. Mag-

netic properties for quasicrystals were extensively studied in a variety of Al–Mn based quasicrystals and Mn–Mn interactions were counted as one of the possible origins for their properties [7–10]. Since an Al_3Mn -type approximant for the Al–Mn–Ge decagonal quasicrystal also indicated a large magnetization anisotropy [9], we carried out the structural analysis of the Al_3Mn -type approximant in this ternary alloy system.

The diffraction patterns of the title compound are quite similar to those of the typical Al_3Mn phase including the systematic absences of $k + l = 2n$ for the $0kl$ plane and $h = 2n + 1$ for the $hk0$ plane [3–6]. These results readily lead the space group of *Pnma* or *Pn2₁a*. The converged parameters in the non-centrosymmetric *Pn2₁a* model serve no significant differences from those in the *Pnma* model, and present analysis selects the centrosymmetric space group *Pnma*. It is usually difficult to determine the distribution of three elements by using the diffraction data alone. Nevertheless, we can obtain here one of the most feasible distribution models as follows. The electron density distribution and corresponding first nearest neighbor distances indicate that Mn1, Mn2, Mn3, Mn4, Mn/Al5, Mn/Al6 and Mn7 are almost fully occupied by Mn. The highest electron density was observed at Ge/Al25 and Ge is suggested to reside here. Mn/Al8, Mn9, Mn/Al15 and Mn/Al16 are coordinated by Ge/Al25 with distances from $2.51 \text{ \AA}$ to $2.58 \text{ \AA}$, suggesting the preference of the smallest Mn at these sites, again. The fundamental preference of Al at remaining thirteen sites was revealed and interatomic distances among them lie over $2.66 \text{ \AA}$, except for $d(\text{Al/Ge18}—\text{Al/Ge18}) = 2.276(3) \text{ \AA}$. Taking into account such features, the structure of the title compound was refined starting from the structural model of Al_3Mn with chemically disordered eleven Mn/Al sites and fourteen Al/Ge sites. Several least-squares iterations revealed the chemically ordered sites of Mn1, Mn2, Mn3, Mn4, Mn7, Mn9, Al10 and Al14. Final results include the restrictions of the chemical composition ratio determined by the electron probe micro analysis. Since the short distance for the Al18—Al18 pair is well reproduced in the Al_3Mn structure [3–5], the unusual Al/Ge18—Al/Ge18 distance for the title compound may be attributed to the partial distribution of Ge together with small coordination polyhedra of Mn1 at both ends of this pair.

The crystal structure of the title compound consists of pentagonal columnar arrangements running parallel to the *b* axis. The atomic distribution of such pentagonal columns can be readily implied in order to reproduce the structure of decagonal quasicrystals. A number of Mn—Mn pairs with the distance less than $2.8 \text{ \AA}$ are located on the mirror plane perpendicular to the *b* axis and a pentagonal atomic arrangement of Mn3—Mn4—Mn/Al6—Mn2—Mn/Al5 could be found, in particular. It is quite natural to attribute such a Mn pentagon to the origin of the easy magnetization axis in the (010) plane of the title compound and quasiperiodic plane of the corresponding decagonal phase.

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Table 1. Data collection and handling.

Crystal:	black, irregular, size 0.03 × 0.06 × 0.09 mm
Wavelength:	Mo K_{α} radiation (0.71069 Å)
μ :	171.19 cm ⁻¹
Diffractometer, scan mode:	Bruker AXS SMART APEX-II CCD, ψ/ω
$2\theta_{\max}$:	55.68°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	12674, 2786
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2120
$N(\text{param})_{\text{refined}}$:	211
Programs:	SHELXL-97 [12], ATOMS [13]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Mn(1)	4c		0.04068(8)	¼	−0.14804(9)	0.0130(6)	0.0070(6)	0.0080(6)	0	0.0017(5)	0
Mn(2)	4c		0.23014(8)	¼	0.17001(9)	0.0068(6)	0.0044(5)	0.0098(6)	0	−0.0009(4)	0
Mn(3)	4c		0.05531(8)	¼	0.45412(9)	0.0073(6)	0.0041(5)	0.0055(5)	0	−0.0005(4)	0
Mn(4)	4c		0.22653(8)	¼	0.51971(9)	0.0089(6)	0.0051(5)	0.0084(6)	0	−0.0001(4)	0
Mn(5)	4c	0.845(3)	0.05315(9)	¼	0.2383(1)	0.0150(7)	0.0097(7)	0.0135(7)	0	0.0011(5)	0
Mn(6)	4c	0.865(9)	−0.16184(9)	¼	0.1561(1)	0.0139(7)	0.0093(7)	0.0110(7)	0	0.0009(5)	0
Mn(7)	8d		−0.18093(6)	0.44292(6)	0.65496(6)	0.0072(4)	0.0033(4)	0.0059(4)	0.0000(3)	0.0003(3)	0.0005(3)
Mn(8)	8d	0.959(6)	−0.18080(6)	0.43861(7)	0.03953(7)	0.0127(5)	0.0090(5)	0.0109(5)	0.0009(3)	−0.0010(3)	−0.0001(3)
Mn(9)	8d		0.12648(6)	0.43786(7)	0.15517(7)	0.0105(4)	0.0093(4)	0.0116(5)	−0.0005(3)	0.0009(3)	−0.0002(3)
Al(10)	4c		0.0938(2)	¼	0.6590(2)	0.008(1)	0.014(1)	0.005(1)	0	0.0008(9)	0
Ge(11)	4c	0.304(6)	−0.1035(1)	¼	−0.0427(1)	0.0114(9)	0.036(1)	0.0120(9)	0	0.0019(7)	0
Ge(12)	4c	0.349(6)	0.1051(1)	¼	0.0360(1)	0.0135(9)	0.041(1)	0.0112(9)	0	−0.0019(6)	0
Ge(13)	4c	0.099(6)	0.4013(1)	¼	0.1421(2)	0.006(1)	0.022(1)	0.011(1)	0	0.0011(8)	0
Al(14)	4c		0.3158(2)	¼	−0.1589(2)	0.024(2)	0.005(1)	0.023(2)	0	−0.005(1)	0
Mn(15)	8d	0.737(6)	0.01180(7)	0.43735(8)	0.35176(8)	0.0143(6)	0.0100(6)	0.0126(6)	−0.0011(4)	0.0004(4)	0.0002(4)
Mn(16)	8d	0.662(6)	−0.18583(7)	0.43487(8)	0.27715(9)	0.0160(6)	0.0092(6)	0.0132(6)	0.0000(4)	0.0011(4)	0.0006(4)
Ge(17)	8d	0.146(4)	0.1280(1)	0.4376(1)	0.5336(1)	0.0100(7)	0.0087(7)	0.0130(8)	−0.0005(5)	−0.0013(5)	0.0013(5)
Ge(18)	8d	0.130(1)	−0.4868(1)	0.4205(1)	0.5421(1)	0.041(1)	0.0186(8)	0.0168(8)	−0.0007(7)	−0.0086(7)	0.0022(6)
Ge(19)	8d	0.490(4)	0.18135(6)	0.35641(7)	0.34408(7)	0.0137(5)	0.0068(5)	0.0118(5)	−0.0004(3)	−0.0001(3)	0.0004(3)
Ge(20)	8d	0.307(4)	−0.22895(8)	0.38753(9)	−0.15787(8)	0.0129(6)	0.0152(6)	0.0070(6)	−0.0025(5)	0.0021(4)	0.0039(4)
Ge(21)	8d	0.107(4)	−0.0498(1)	0.3774(1)	0.5436(1)	0.0095(8)	0.0129(8)	0.0096(8)	0.0033(6)	0.0034(5)	−0.0025(6)
Ge(22)	8d	0.225(4)	−0.23756(9)	0.3840(1)	0.4742(1)	0.0142(7)	0.0149(7)	0.0099(7)	−0.0005(5)	−0.0029(5)	−0.0047(5)
Ge(23)	8d	0.328(4)	−0.04669(8)	0.38618(9)	−0.23911(9)	0.0144(6)	0.0150(6)	0.0192(7)	0.0065(5)	−0.0052(4)	−0.0015(5)
Ge(24)	8d	0.245(4)	0.15682(9)	0.3859(1)	−0.1656(1)	0.0108(7)	0.0153(7)	0.0273(8)	−0.0047(5)	−0.0026(5)	−0.0038(5)
Ge(25)	8d	0.934(4)	−0.04355(4)	0.40122(6)	0.15724(5)	0.0071(4)	0.0196(4)	0.0152(4)	−0.0019(3)	−0.0025(2)	0.0066(3)
Al(5)	4c	0.155(3)	0.05315(9)	¼	0.2383(1)	0.0150(7)	0.0097(7)	0.0135(7)	0	0.0011(5)	0
Al(6)	4c	0.135(9)	−0.16184(9)	¼	0.1561(1)	0.0139(7)	0.0093(7)	0.0110(7)	0	0.0009(5)	0
Al(8)	8d	0.041(6)	−0.18080(6)	0.43861(7)	0.03953(7)	0.0127(5)	0.0090(5)	0.0109(5)	0.0009(3)	−0.0010(3)	−0.0001(3)
Al(11)	4c	0.696(6)	−0.1035(1)	¼	−0.0427(1)	0.0114(9)	0.036(1)	0.0120(9)	0	0.0019(7)	0
Al(12)	4c	0.651(6)	0.1051(1)	¼	0.0360(1)	0.0135(9)	0.041(1)	0.0112(9)	0	−0.0019(6)	0
Al(13)	4c	0.901(6)	0.4013(1)	¼	0.1421(2)	0.006(1)	0.022(1)	0.011(1)	0	0.0011(8)	0
Al(15)	8d	0.263(6)	0.01180(7)	0.43735(8)	0.35176(8)	0.0143(6)	0.0100(6)	0.0126(6)	−0.0011(4)	0.0004(4)	0.0002(4)
Al(16)	8d	0.338(6)	−0.18583(7)	0.43487(8)	0.27715(9)	0.0160(6)	0.0092(6)	0.0132(6)	0.0000(4)	0.0011(4)	0.0006(4)
Al(17)	8d	0.854(4)	0.1280(1)	0.4376(1)	0.5336(1)	0.0100(7)	0.0087(7)	0.0130(8)	−0.0005(5)	−0.0013(5)	0.0013(5)
Al(18)	8d	0.870(1)	−0.4868(1)	0.4205(1)	0.5421(1)	0.041(1)	0.0186(8)	0.0168(8)	−0.0007(7)	−0.0086(7)	0.0022(6)
Al(19)	8d	0.510(4)	0.18135(6)	0.35641(7)	0.34408(7)	0.0137(5)	0.0068(5)	0.0118(5)	−0.0004(3)	−0.0001(3)	0.0004(3)
Al(20)	8d	0.693(4)	−0.22895(8)	0.38753(9)	−0.15787(8)	0.0129(6)	0.0152(6)	0.0070(6)	−0.0025(5)	0.0021(4)	0.0039(4)
Al(21)	8d	0.893(4)	−0.0498(1)	0.3774(1)	0.5436(1)	0.0095(8)	0.0129(8)	0.0096(8)	0.0033(6)	0.0034(5)	−0.0025(6)
Al(22)	8d	0.775(4)	−0.23756(9)	0.3840(1)	0.4742(1)	0.0142(7)	0.0149(7)	0.0099(7)	−0.0005(5)	−0.0029(5)	−0.0047(5)
Al(23)	8d	0.672(4)	−0.04669(8)	0.38618(9)	−0.23911(9)	0.0144(6)	0.0150(6)	0.0192(7)	0.0065(5)	−0.0052(4)	−0.0015(5)
Al(24)	8d	0.755(4)	0.15682(9)	0.3859(1)	−0.1656(1)	0.0108(7)	0.0153(7)	0.0273(8)	−0.0047(5)	−0.0026(5)	−0.0038(5)
Al(25)	8d	0.066(4)	−0.04355(4)	0.40122(6)	0.15724(5)	0.0071(4)	0.0196(4)	0.0152(4)	−0.0019(3)	−0.0025(2)	0.0066(3)

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