

Structure Refinement of the Iron–Aluminium Phase with the Approximate Composition Fe_2Al_5

BY U. BURKHARDT, YU. GRIN AND M. ELLNER

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Seestrass 92, D-70174 Stuttgart, Germany

AND K. PETERS

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70506 Stuttgart, Germany

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Abstract

Diiron pentaaluminide, Fe_2Al_5 , $M_r = 268.8$, orthorhombic, $Cmcm$ (No. 63), $a = 7.6559$ (8), $b = 6.4154$ (6), $c = 4.2184$ (4) Å, $V = 207.19$ (6) Å³, $Z = 2$, $D_x = 4.23$ (2), $D_m = 4.20$ (1) Mg m⁻³, Mo $K\alpha$ radiation, $\mu = 8.2$ mm⁻¹, $F(000) = 249.6$, $T = 293$ K, $R = 0.0229$, $wR = 0.0270$ for 137 unique reflections. The refined structure differs from the approximate structure proposed previously by an additional partially occupied atomic position.

Introduction

According to the phase diagram of Fe–Al (Massalski, Okamoto, Subramanian & Kacprzak, 1990), the Fe_2Al_5 phase forms congruently at 1442 K and has a homogeneity range between 70 and 73 at.% Al. The approximate crystal structure of this phase was originally proposed by Schubert, Rösler, Kluge, Anderko & Härle (1953): space group $Cmcm$, $a = 7.675$, $b = 6.403$, $c = 4.203$ Å. Later, the structure of Fe_2Al_5 was compared with MnAl_6 (Schubert & Kluge, 1953) and also Co_2Al_5 (Schubert, 1964), which is homeotypic with Fe_2Al_5 . More recently, lattice parameters of Fe_2Al_5 were also reported by Griger, Stefániay & Turmezey (1986).

X-ray and electron-diffraction investigations performed on the splat-cooled samples confirmed the unit-cell geometry, but a set of reflections was found in electron-diffraction patterns which did not conform with the space group $Cmcm$ (Ellner & Mayer, 1992).

The aim of the present work was to investigate the stability of the Fe_2Al_5 phase in the temperature range $T = 293$ – 1228 K and to refine the crystal structure of Fe_2Al_5 .

Experimental

To prepare an alloy with the composition $\text{Fe}_{28.5}\text{Al}_{71.5}$, the two elements with purity Fe $m3n8$ (Alfa Products) and Al 99.999% (Heraeus) were melted in an arc furnace under 10^{-3} bar argon (Messer–Griesheim 5.0) pressure. The total mass of the alloy was *ca* 4 g. As the mass loss

during melting was less than 1%, no chemical analysis was carried out. Then, to obtain a microhomogeneous sample, the alloy was wrapped in a thin molybdenum foil, enclosed in an evacuated silica tube and annealed at 1120 K for 2 d. This annealing temperature was based on the formation temperature of the compound investigated and chosen to avoid mass loss of aluminium during heat treatment. Both the annealed and the as-cast alloys were investigated with metallographic methods to determine the homogeneity and grain size. The macroscopic density of the $\text{Fe}_{28.5}\text{Al}_{71.5}$ sample was determined by the buoyancy method [hydrostatic method (Marton, 1959)] using CCl_4 at $T = 293$ K.

The powder diffraction experiments were carried out on an Enraf–Nonius FR552 Guinier camera. To obtain a high resolution on the one hand and a suitable number of diffraction lines on the other, $\text{Co } K\alpha_1$, $\text{Fe } K\alpha_1$ and $\text{Cr } K\alpha_1$ radiation were used. The photographs were calibrated with silicon or germanium. The reflection positions on the Guinier photographs were measured with a Line-Scanner LS-20. The lattice parameters were refined with least-squares calculations using all observed diffraction peaks. For the high-temperature X-ray powder diffraction measurements, an Enraf–Nonius FR553 Guinier–Simon camera with $\text{Fe } K\alpha_1$ radiation was used. These photographs were evaluated by means of an Abbe comparator.

For the crystal structure investigation, single-crystal fragments with a mean dimension of 0.2 mm were selected from the crushed annealed alloy. Rotation and Weissenberg photographs were taken with Mo $K\alpha$ and $\text{Co } K\alpha$ radiation. The intensity data of 312 reflections were collected on a Syntex $P\bar{1}$ four-circle automatic diffractometer (Mo $K\alpha$ radiation, graphite monochromator) in the θ - 2θ mode ($-8 \leq h \leq +8$, $-9 \leq k \leq +9$, $0 \leq l \leq 5$) up to $(\sin \theta/\lambda)_{\text{max}} = 0.65$ Å⁻¹. In respect of the small size of the sample, no measurements were made when $\sin \theta/\lambda \geq 0.65$ Å⁻¹. The absorption correction was performed by means of a ψ -scan algorithm using the intensities of six standard reflections (200, 400, 600, 530, 311 and 221). The maximal and minimal trans-

mission factors are 0.085 and 0.072, respectively. After the elimination of weak [$|F| < 4\sigma(F)$] and averaging of symmetry-dependent reflections, a set of 137 reflections was obtained for the structure refinement. No remarkable increase of the number of usable reflections was obtained by application of the lower limit value [142 reflections with $|F| < 2\sigma(F)$].

Lattice-parameter refinement, structure solution, structure refinement and graphical presentation were performed using the *CSD* program package (Akselrud, Grin, Zavalii, Pecharsky & Fundamenski, 1989).

Results

The micrograph of the Fe_{28.5}Al_{71.5} sample had a homogeneous pattern with an average grain size of approximately 100 μm before annealing. On heat treatment, the grain size increases to an average value of 200 μm .

Guinier photographs of the as-cast alloy and the annealed alloy Fe_{28.5}Al_{71.5} only contained diffraction lines of the Fe₂Al₅ structure. Diffraction patterns were indexed on the basis of an orthorhombic *C*-centred unit cell, which agrees with the structure proposed for Fe₂Al₅ by Schubert, Rösler, Kluge, Anderko & Härle (1953). The refined lattice parameters are $a = 7.6559(8)$, $b = 6.4154(6)$, $c = 4.2184(4)$ Å.

The temperature dependence of the lattice parameters determined for the Fe_{28.5}Al_{71.5} sample using nine diffraction lines is given in Fig. 1. In agreement with the result of the micrograph analysis, no phase transition was observed.

The single-crystal fragments of irregular shape suitable for structure investigation were separated from the crushed annealed alloy, because of the increase in grain size after heat treatment.

The dimensions of the unit cell and the systematic absences of reflections were verified by the rotation

photographs with [001] rotation axes and Weissenberg photographs of the projections (hhl) and ($h, h + 2l, l$). The Weissenberg photographs show the limiting conditions $l = 2n$ for $h0l$ reflections and $h + k = 2n$ for hkl reflections. Additional strip-like diffuse reflections characteristic of partially disordered structures were observed in the ($h, h + 2l, l$) zone. These reflections have the non-integer indices $l = 3/2$ and $l = 5/2$. Such reflections with $l = 1/2$ were also observed in the ($h, h + 2l, l$) projection of electron-diffraction patterns obtained from splat-cooled samples by Ellner & Mayer (1992).

The systematic absences observed in the collected diffractometer data described above conform with the following space groups: *Cmcm*, *Cmc2₁* and *C2cm* [conventional setting *Ama2*; *International Tables for X-ray Crystallography* (1989, Vol. A)].

The structure refinement was carried out in the space group *Cmcm* by the use of structure factors for 137 reflections ($|F| > 4\sigma|F|$) collected on an automatic four-circle diffractometer. A one-parameter Sheldrick model for extinction correction was used [extinction parameter equal to 0.0046(9)]. The fit of 13 parameters in the isotropic approximation gave the R_F value of 0.068 and anisotropic approximation of the thermal displacements with 24 parameters led to the final values of $R = 0.0229$ and $wR = 0.0270$ [$S = 1.03$, $w = 1/\sigma^2(|F|)$]. The significance of the anisotropic approximation was checked using the Hamilton test (Hamilton, 1965).* Occupation parameters were refined together with the thermal parameters with a fixed scale factor.

No strong correlations were found between the occupation parameters and thermal parameters for Al2 and Al3 positions. The final maximal and minimal residual electron-density values were +0.5 and -0.5 e Å⁻³. Atomic position and displacement parameters are given in Table 1 and interatomic distances are shown in Table 2. The refinement of the structure in the other space groups *Cmc2₁* and *C2cm* did not lead to significantly better R values (0.021 for 29 variable parameters in *Cmc2₁* and 0.022 for 34 variable parameters in *C2cm*). Also, the anisotropic thermal displacement for Al2 and Al3 atoms could not be refined with satisfaction in the last two space groups.

The refined structure contains 15.2(0.32) atoms per unit cell. The calculated density value is $\rho_{\text{ts}} = 4.23(2)$ Mg m⁻³. This value conforms with the result of the experimental density measurements of $\rho_{\text{exp}} = 4.20(1)$ Mg m⁻³.

The aluminium content of the refined structure $x_{\text{Al}}^{\text{ts}} = 0.737(5)$ mole fraction is roughly 2 at.% greater than the initial value $x_{\text{Al}}^{\text{i}} = 0.715(3)$ (the deviation arises from mass loss during sample preparation). This difference

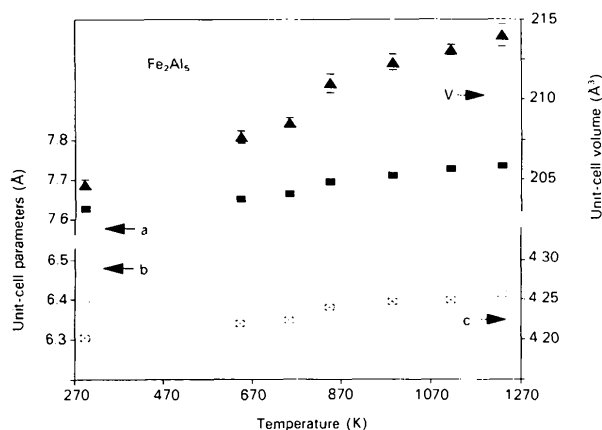


Fig. 1. Unit-cell parameters versus temperature for Fe₂Al₅ (■ - *a* parameter, □ - *b* parameter, ∅ - *c* parameter, ▲ - unit-cell volume, horizontal bars define the standard deviations).

* The dimension of the hypothesis is $24 - 13 = 11$ and the number of degrees of freedom for the refinement is $137 - 24 = 113$. The appropriate R -factor ratio, $R = R_{\text{iso}}/R_{\text{aniso}} = 2.97$, is much larger than the tabular value $R_{11,113,0.005} = 1.14$.

Table 1. Atomic parameters for Fe_2Al_5

$$B_{\text{eq}} = (1/3)[B_{11}(a_1^*)^2(a_1)^2 + \dots + 2B_{23}a_2^*a_3^*a_2a_3\cos\alpha]$$

	Site	x	y	z	B_{eq}	
4Fe	4(c)	0	0.8277 (1)	1/4	1.01 (2)	
8Al1	8(g)	0.1880 (2)	0.1467 (2)	1/4	1.50 (3)	
4Al2†	4(b)	0	1/2	0	1.3 (5)	
8Al3†	8(f)	1/2	0.034 (2)	0.830 (7)	2.1 (6)	
	B11	B22	B33	B12	B13	B23
4Fe	0.80 (4)	0.85 (4)	1.37 (4)	0	0	0
8Al1	1.34 (6)	2.21 (7)	0.94 (5)	-0.80 (5)	0	0
4Al2	0.9 (3)	1.2 (4)	1.8 (14)	0	0	1.1 (5)
8Al3	1.6 (3)	1.3 (3)	3.4 (17)	0	0	-1.0 (4)

† Occupations: Al2 = 0.32 (4) Al; Al3 = 0.24 (2) Al.

Table 2. Interatomic distances less than 3.1 Å in Fe_2Al_5 (Å)

Fe—2Al3	2.34 (2)	Al2—2Al3	0.75 (3)
Fe—2Al2	2.352 (1)	Al2—2Al3	1.41 (3)
Fe—2Al1	2.502 (2)	Al2—2Al2	2.1092 (4)
Fe—4Al1	2.559 (1)	Al2—2Fe	2.352 (1)
Fe—2Al3	2.59 (2)	Al2—4Al1	2.776 (2)
Fe—2Al1	2.656 (2)	Al2—2Al3	2.84 (6)
Fe—2Fe	3.055 (1)	Al2—4Al1	2.884 (2)
Fe—2Al3	3.09 (3)		
Al1—Fe	2.502 (2)	Al3—Al3	0.67 (4)
Al1—2Al3	2.53 (1)	Al3—Al2	0.75 (3)
Al1—2Fe	2.559 (1)	Al3—Al2	1.41 (3)
Al1—Fe	2.656 (2)	Al3—Al3	1.50 (4)
Al1—2Al1	2.666 (1)	Al3—2Al3	2.15 (4)
Al1—2Al3	2.676 (8)	Al3—Fe	2.35 (4)
Al1—2Al2	2.776 (2)	Al3—2Al1	2.53 (1)
Al1—2Al1	2.827 (2)	Al3—Fe	2.59 (2)
Al1—Al1	2.878 (2)	Al3—2Al1	2.676 (8)
Al1—2Al2	2.884 (2)	Al3—Al3	2.82 (4)
Al1—2Al3	3.06 (2)	Al3—Al2	2.84 (3)
		Al3—2Al1	3.06 (2)
		Al3—Fe	3.09 (3)

can be explained either by the absorption not being corrected fully in an irregularly shaped crystal or by the partial occupation of the Al2 and Al3 sites by Fe atoms. From the analysis of the X-ray diffraction data it is not possible to distinguish between Fe and Al atoms in the low-occupied sites.

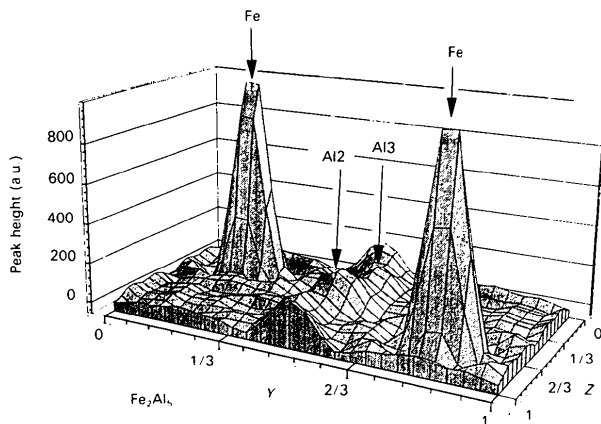


Fig. 2. Fourier map for the (100) plane in the Fe_2Al_5 structure. The intensity of the peaks is given in arbitrary units.

Discussion

The refined structure of Fe_2Al_5 differs from the former approximate structure proposal in the distribution of the Al atoms in the (100) plane. The partially disordered distribution of atoms is a special feature of the Fe_2Al_5 structure. The Al atom at 0,0.5,0 (Al2) from the earlier structure proposal did not fully describe the electron-density distribution in this plane (Fig. 2). Besides the large Fe-atom peaks, the electron-density map in the (100) plane contains a chain of small overlapped maxima in the region around $y = 0.5$. For the correct description of this region, at least one additional atom is necessary (Al3) in the 8(f) position. The Al2 and

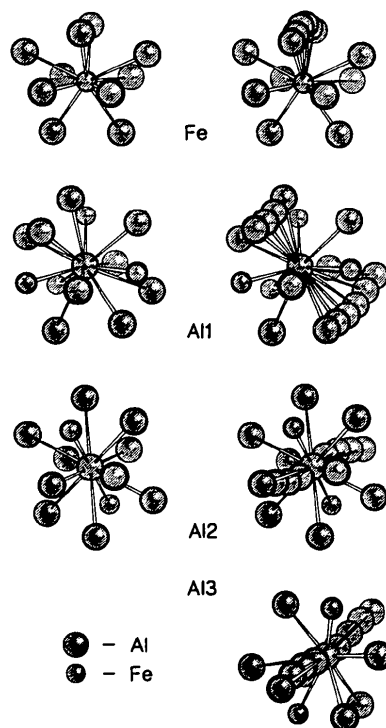


Fig. 3. The environment of the atoms in the ideal (left) and real (right) Fe_2Al_5 structure.

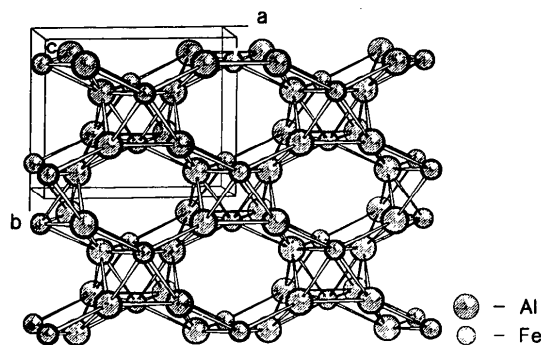


Fig. 4. Three-dimensional framework of Fe and Al1 atoms in the Fe_2Al_5 structure.

Al3 positions deviate considerably from full occupancy, with the occupation factors 0.36 and 0.23, respectively. Remarkable anisotropy of thermal motion of Al2 and Al3 atoms (*B*₃₃ is larger than *B*₁₁ and *B*₂₂) correlates with the electron-density distribution in the (100) plane (see Fig. 2). The Fe and Al1 atoms are placed in the same positions, as in the former approximate structure proposal.

The partial occupation of aluminium positions Al2 and Al3 in the Fe₂Al₅ structure leads to a different atomic coordination compared with the former proposal (Fig. 3). Some edges of coordination polyhedra became more diffuse with respect to the non-ordered location of atoms on them. The coordination polyhedron of the Fe atom has one such edge, the coordination polyhedron of the Al1 atom has two. The coordination figures of Al2 and Al3 atoms are comparable with the coordination polyhedron of the Al2 atom in the former model, if the overlapping atoms were excluded from the coordination sphere.

One of the possible reasons for the non-ordered distribution of Al atoms along the [001] axis could arise from interactions of Fe and Al1 atoms, which build the three-dimensional framework with the channels located along the [001] axis (Fig. 4). The interatomic distances between atoms building this framework are from 2.5 to 2.66 Å and are *ca* 8% shorter than the sum of atomic radii ($r_{\text{Fe}} + r_{\text{Al}} = 2.69 \text{ \AA}$, $2r_{\text{Al}} = 2.86 \text{ \AA}$). The channels have the shape of pentagonal antiprisms and are connected

by side edges. There are two types of points on the axes of the channels; atoms on these points presumably have more stronger interactions with the Fe atoms from the framework (the respective distances between the Fe atoms and these points are *ca* 2.36 Å). In fact, both positions are occupied by the Al atoms (Al2 and Al3). As the positions are very close to each other (see Table 2), both of them cannot be occupied at the same time and consequently the occupation of these sites is incomplete.

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The Synergetic Effect in Beryllium Sulfate Tetrahydrate – an Experimental Electron-Density Study*

BY THOMAS KELLERSOHN†

Anorganische Chemie I, Universität GH Siegen, Postfach 101240, D-57068 Siegen, Germany

AND ROBERT G. DELAPLANE AND IVAR OLOVSSON‡

Department of Inorganic Chemistry, Institute of Chemistry, Uppsala University, Box 531, S-751 21 Uppsala, Sweden

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Dedicated to Professor H. D. Lutz on the occasion of his 60th birthday

Abstract

The electron density in piezoelectric beryllium sulfate tetrahydrate has been determined by multipole

refinement of single-crystal X-ray data collected at 30 K. Hydrogen positional and displacement parameters have been taken from a refinement using single-crystal neutron data. Structural parameters are also given based on single-crystal neutron data collected at 100 and 295 K. The Be²⁺ ion causes a strong polarization of the lone-pair density of the water O atom. Only a single maximum of the deformation density is observed in this region. The polarization is

* Hydrogen Bond Studies. 158. Part 157: Kellersohn, Delaplane, Olovsson & McIntyre (1993).

† Present address: Editorial Department, VCH Publishers, Postfach 101161, D-69451 Weinheim, Germany.

‡ To whom correspondence should be addressed.