

## Aluminium – Cerium – Iron

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### Literature Data

The first investigation in this ternary system was made in 1925 by Meißner [1925Mei] to describe the “clear-cross method” of Guertler in practical examples when Ce is added to Al-Fe alloys. [1969Zar] examined the ternary system with 106 alloys from 0 to 33.3 at.% Ce using X-ray structural analysis. [1988Sok] studied the phase behavior of 75 to 100 at.% Al at 550°C using X-ray structural analysis. An isothermal section for the Al-rich corner at the same temperature is presented by [1992Rae] without specifying sample preparation details and the purity of the starting materials. Their results are in good agreement. Solid solutions of Al in binary Ce-Fe phases became of interest with a view to obtaining a material with good permanent magnetic properties after the discovery of rare-earth metal (R)-transition metal (TM) magnets. [1985Fra] published lattice parameters and magnetic properties of alloys along  $\text{CeFe}_2\text{-CeAl}_2$ . [1998Kuc, 2000Kny] measured the structural, magnetic and optical properties of a  $\text{Ce}_2\text{Fe}_{15.3}\text{Al}_{1.7}$ . Samples were prepared by levitation melting in an induction furnace, annealed at 1000°C for 8h and analyzed by X-ray diffraction and a vibrating sample magnetometer. No information of the purity of the starting material is given. The structural and magnetic properties of  $\text{RE}_2\text{Fe}_{17-x}\text{Al}_x$  phases have been reviewed and compared by [2002Ram]. A new ternary phase with the composition  $\text{Ce}_6\text{Fe}_{11}\text{Al}_3$  has been discovered recently [1992Hu]. The sample has been prepared by melting the elements (Ce, Fe 3N purity, Al 5N) followed by an anneal for 120h at 600 - 800°C wrapped in Mo foil and sealed in quartz. The water quenched samples have been investigated by XRD and Mössbauer spectroscopy to determine the magnetic properties. The structure and magnetic properties of  $\text{CeFe}_2\text{Al}_8$  have been studied by low temperature neutron diffraction [2001Kol] and Mössbauer spectroscopy by [2000Tam, 2001Kol]. No magnetic ordering of this compound has been detected. Ce enhances the mechanical properties of Fe-Al alloys. Because of the very limited solid solubility of transition metals and rare-earth elements in Al rapid solidification processing of Al alloys with Fe and Ce is necessary to avoid intermetallic compounds. [1986Ang, 1986Fie, 1986Jha, 1987Yan, 1988Aye, 1988Sok, 1998Fas, 2000Cha, 2002Zha] produced and investigated rapidly solidified Al-Ce-Fe alloys and found besides binary Fe-Al phases, stable and metastable ternary phases. Enthalpies of formation of three-component liquid alloys were published by [1984Esi].

This evaluation proceeds that of [1991Gri] and integrates the substantial amount of data published since then.

### Binary Systems

The Al-Fe binary system has been taken from [2003Pis]. [1996Sac] revised the Al-Ce system and their diagram is accepted. The Al-rich compound in the Al-Ce system, previously reported as  $\text{CeAl}_4$ , is now known to have the  $\text{Ce}_3\text{Al}_{11}$  stoichiometry. The composition  $\text{CeAl}_4$  taken by [1969Zar] is corrected to  $\text{Ce}_3\text{Al}_{11}$  in the ternary evaluation and in Fig. 1. Ce-Fe is accepted from [Mas].

### Solid Phases

The ternary phase  $\text{CeFe}_4\text{Al}_8$  ( $\tau_1$ ) has been studied in detail [1961Gla, 1962Zar, 1969Zar, 1974Viv, 1976Bus]. [1969Zar] found additionally the ternary phases  $\text{CeFe}_2\text{Al}_{10}$  ( $\tau_2$ ),  $\text{CeFe}_2\text{Al}_7$ ,  $\text{CeFe}_{1-1.4}\text{Al}_{1-0.6}$  and a solid solution of Al in the binary  $\text{Ce}_2\text{Fe}_{17}$  compound with a maximum Al-content of about 60 at.% and having a  $\text{Th}_2\text{Ni}_{17}$  type structure.  $\text{CeFe}_2\text{Al}_{10}$  ( $\tau_2$ ) is iso-structural to  $\text{YbFe}_2\text{Al}_{10}$  [1998Thi]. The lattice parameters of the  $\tau_3$   $\text{Ce}_6\text{Fe}_{11}\text{Al}_3$  ternary compound has been determined by [1992Hu]. This compound has a  $\text{La}_6\text{Fe}_{11}\text{Ga}_3$  type structure. The structures of  $\text{CeFe}_2\text{Al}_7$ , and  $\text{CeFe}_{1-1.4}\text{Al}_{1-0.6}$  were not determined. The ternary phase  $\text{CeFe}_2\text{Al}_7$  is possibly identical to  $\tau_1$   $\text{CeFe}_2\text{Al}_8$ , observed and investigated by [1974Yar]. According to [1971Oes], the compounds of the composition  $\text{RFeAl}$  with light rare-earths show a two phase region of  $cF24$  ( $\text{MgCu}_2$ ) type together with an unidentified second phase, as opposed to all alloys  $\text{RFeAl}$

with heavy rare-earths which form a single phase of the hexagonal *hP*12 (MgZn<sub>2</sub>) structure type. The formation of successive types of the Laves phase family in the pseudobinary system RFe<sub>2</sub>–RAl<sub>2</sub> seems to be connected with Fermi surface–Brillouin zone interactions. It is not completely understood, however, why this does not hold for light and heavy rare-earth elements together, but it is likely that the larger size and higher valencies of the former may contribute to their exceptional behavior. [1985Fra] suggests that the solubility limit for the formation of the pure MgCu<sub>2</sub> type structure for Ce(Fe<sub>1–x</sub>Al<sub>x</sub>)<sub>2</sub> may be placed near  $x = 0.125$ . [1986Ang] found five dispersed phases in the as-extruded Al–8.8Fe–3.7Ce and Al–8.9Fe–6.9Ce alloys; metastable FeAl<sub>6</sub>, two metastable Al–Ce–Fe phases and the equilibrium phases Fe<sub>4</sub>Al<sub>13</sub> and CeFe<sub>2</sub>Al<sub>10</sub>. The unit cell of one of the metastable ternary phases was observed as orthorhombic. [1987Yan] produced a metastable icosahedral phase in rapidly cooled Al–8.8Fe–3.3Ce. In addition [1988Aye] found two compounds  $\tau_2$  CeFe<sub>2</sub>Al<sub>10</sub> and CeFe<sub>5</sub>Al<sub>20</sub> in the as-extruded conditions. CeFe<sub>5</sub>Al<sub>20</sub> is described as decagonal quasicrystal. The known structure types and crystal parameters of all described solid phases are listed in Table 1. The ternary phase CeFe<sub>2</sub>Al<sub>8</sub> listed by [V–C] with the source [1980Zar] is not described in the latter paper. [1980Zar] investigated the phase CeCo<sub>2</sub>Al with structure type CeFe<sub>2</sub>Al<sub>8</sub>. The lattice parameters in [V–C] are those of CeCo<sub>2</sub>Al<sub>8</sub>.

### Invariant Equilibria

The formation of  $\tau_2$  follows the peritectic reaction  $\text{Ce}_3\text{Al}_{11} + \text{L} \rightleftharpoons \tau_2$ . The formation temperature is 940°C [1988Sok].

### Isothermal Sections

The investigation of [1925Mei] is rather sketchy and incorrect in the region up to 33.3 at.% Ce. The results of [1969Zar] confirmed several ternary compounds and solid solution of Al in Ce<sub>2</sub>Fe<sub>17</sub>. Figure 1 shows the phase equilibria of the ternary system at 500°C with a maximum Ce content of 33.3 at.%. CeFe<sub>2</sub> is printed by [1969Zar] as  $\alpha$  phase with no Al solubility. This is corrected in the figure after the results of [1985Fra]. The phase, CeFe<sub>1.4</sub>Al<sub>1.06</sub>, detected by [1969Zar] is plotted, but it is necessary to point out the conflict with the results of [1971Oes] as described above. The phase CeFe<sub>2</sub>Al<sub>7</sub> of [1969Zar] is printed with the composition  $\tau_1$  CeFe<sub>2</sub>Al<sub>8</sub> as in [1974Yar]. At 550°C for Al concentration of 75 to 100 at.% [1988Sok] found the two-phase regions Al+ $\tau_2$ , Al+FeAl<sub>3</sub>, Al+Ce<sub>3</sub>Al<sub>11</sub> and the three phase regions Al+ $\tau_2$ +FeAl<sub>3</sub> and Al+ $\tau_2$ +Ce<sub>3</sub>Al<sub>11</sub>. The ternary compound is not observed in quenched material. The isothermal section in the Al-rich corner at 550°C as presented by [1992Rae] is identical to Fig. 1.

### Temperature – Composition Sections

[1988Sok] published two isopleths. One describes the section between Ce<sub>3</sub>Al<sub>11</sub> and Fe<sub>4</sub>Al<sub>13</sub>, the second between Al and CeFe<sub>2</sub>Al (Fig. 2). The isopleth is taken only partially because the shape of the lines with less than 97.8 at.% Al is estimated. The results are based on thermal analysis. The isopleth between Ce<sub>3</sub>Al<sub>11</sub> and Fe<sub>4</sub>Al<sub>13</sub> is not accepted because of inconsistency with the accepted binary Al–Ce.

### Notes on Materials Properties and Applications

Magnetic properties of  $\tau_2$  CeFe<sub>4</sub>Al<sub>8</sub> samples have been determined and analyzed by [1998Sch, 2000Hag, 2000Sik, 2001Gac] using neutron diffraction, specific heat and Mössbauer measurements. The magnetic properties of a series of Ce<sub>2</sub>Fe<sub>17–x</sub>Al<sub>x</sub> solid solutions with  $x$  equal to 0.0, 0.88, 2.06, 2.80, 3.98, 5.15, 6.08, 7.21, 8.20, 9.08, 9.84, and 10.62 have been studied by magnetic measurements, neutron diffraction, and Mössbauer spectroscopy by [1996Mis] and with  $8 \leq x \leq 13$  by susceptibility, magnetization and heat capacity measurements by [2000Kon]. The Curie temperature increases from 238 K in Ce<sub>2</sub>Fe<sub>17</sub> to a maximum of 284 K in Ce<sub>2</sub>Fe<sub>14</sub>Al<sub>3</sub>. The Ce<sub>2</sub>Fe<sub>17–x</sub>Al<sub>x</sub> solid solutions behave as spin glasses for  $x$  greater than 7 [1996Mis]. The magnetic moment of Ce<sub>2</sub>Fe<sub>15.3</sub>Al<sub>1.7</sub> has been measured as  $M_s = 25.68 \mu_B$  [2001Kny]. The origin for the magnetism of  $\tau_2$  CeFe<sub>2</sub>Al<sub>10</sub> is the mixed Ce<sup>3+</sup>/Ce<sup>4+</sup> valence [1998Thi]. Ce(Fe,Al)<sub>2</sub> with an aluminium content of 6 at.% has a Curie temperature of 160K and a Néel temperature of 136K [1997Fer]. The hydrogen storing capabilities of Ce(Fe,Al)<sub>2</sub> have been investigated by [1997Spa],

their magnetic properties by [1997Fer]. [2000Cha] investigated  $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$  samples with X-ray absorption spectroscopy (XAS) and confirmed the mixed valence of Ce upon Fe substitution to be the origin of the anomalous magnetic behavior in this alloy.

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**Table 1:** Crystallographic Data of Solid Phases

| Phase /<br>Temperature Range<br>[°C] | Pearson Symbol/<br>Space Group/<br>Prototype       | Lattice Parameters<br>[pm]  | Comments/References                                   |
|--------------------------------------|--|---|---|
| (βAl)                                | <i>hP2</i><br><i>P6<sub>3</sub>/mmc</i><br>Mg      | <i>a</i> = 269.3<br><i>c</i> = 439.8  | at 25°C, 20.5 GPa [Mas2]                              |
| (αAl)<br>< 660.452                   | <i>cF4</i><br><i>Fm<math>\bar{3}m</math></i><br>Cu | <i>a</i> = 404.96   | at 25°C [Mas2]  |
| (εFe)                                | <i>hP2</i><br><i>P6<sub>3</sub>/mmc</i><br>Mg      | <i>a</i> = 246.8<br><i>c</i> = 396.0  | at 25°C, 13 GPa [Mas2]                                |
| (δFe)<br>1538-1394                   | <i>cI2</i><br><i>Im<math>\bar{3}m</math></i><br>W  | <i>a</i> = 293.15   | [Mas2]  |
| (γFe)<br>< 1394-912                  | <i>cF4</i><br><i>Fm<math>\bar{3}m</math></i><br>Cu | <i>a</i> = 364.67   | at 915°C [V-C2, Mas2] dissolves up to 1.2 at.% Al     |
| (αFe)<br>< 912                       | <i>cI2</i><br><i>Im<math>\bar{3}m</math></i><br>W  | <i>a</i> = 286.65<br><i>a</i> = 286.64 to 289.59 0 - 18.8 at.% Al, HT [1958Tay]<br><i>a</i> = 286.60 to 289.99 0 - 19.0 at.% Al, HT [1961Lih]<br><i>a</i> = 286.60 to 290.12 0 - 18.7 at.% Al, 25°C [1999Dub] | at 25°C [Mas2] dissolves up to 45.0 at.% Al at 1310°C |
| (α'Ce)                               | <i>oC4</i><br><i>Cmcm</i><br>αU                    | <i>a</i> = 304.9<br><i>b</i> = 599.8<br><i>c</i> = 521.5  | at 25°C, 5.4 GPa [Mas2]                               |
| (δCe)<br>798-726                     | <i>cI2</i><br><i>Im<math>\bar{3}m</math></i><br>W  | <i>a</i> = 412  | [Mas2]  |
| (γCe)<br>726-61                      | <i>cF4</i><br><i>Fm<math>\bar{3}m</math></i><br>Cu | <i>a</i> = 516.10   | [Mas2]  |
| (βCe)<br>61-(-177)                   | <i>hP4</i><br><i>P6<sub>3</sub>/mmc</i><br>αLa     | <i>a</i> = 368.10<br><i>c</i> = 1185.7  | at 25°C [Mas2]  |

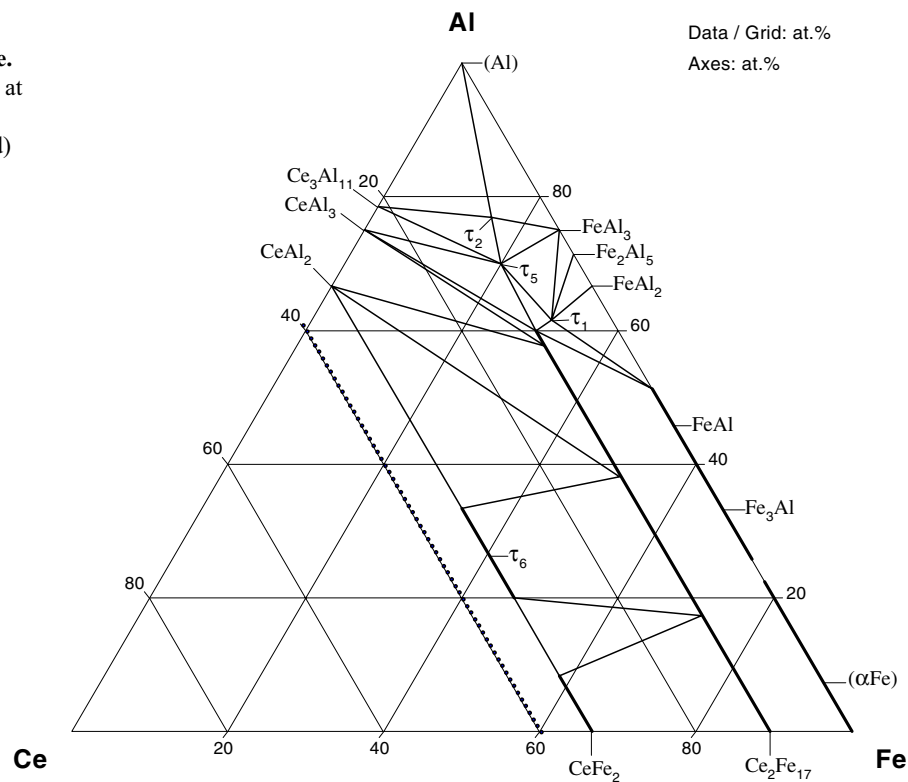
| Phase /<br>Temperature Range<br>[°C]       | Pearson Symbol/<br>Space Group/<br>Prototype                              | Lattice Parameters<br>[pm]   | Comments/References   |
|--|---|--|---|
| ( $\alpha$ Ce)<br>< -177                   | <i>cF4</i><br><i>Fm<math>\bar{3}m</math></i><br>Cu                        | $a = 485$  | [Mas2]  |
| Fe <sub>4</sub> Al <sub>13</sub><br>< 1160 | <i>mC102</i><br><i>C2/m</i><br>Fe <sub>4</sub> Al <sub>13</sub>           | $a = 1552.7$ to $1548.7$<br>$b = 803.5$ to $808.4$<br>$c = 1244.9$ to $1248.8$<br>$\beta = 107.7$ to $107.99^\circ$<br>$a = 1549.2$<br>$b = 807.8$<br>$c = 1247.1$<br>$\beta = 107.69^\circ$ | 74.16 - 76.70 at.% Al, [1986Gri]<br>sometimes called FeAl <sub>3</sub> in the literature<br>at 76.0 at.% Al, [1994Gri]                            |
| Fe <sub>2</sub> Al <sub>5</sub><br>< 1169  | <i>oC24</i><br><i>Cmcm</i><br>-   | $a = 765.59$<br>$b = 641.54$<br>$c = 421.84$   | at 71.5 at.% Al, [1994Bur]  |
| FeAl <sub>2</sub><br>< 1156                | <i>aP18</i><br><i>P1</i><br>FeAl <sub>2</sub>                             | $a = 487.8$<br>$b = 646.1$<br>$c = 880.0$<br>$\alpha = 91.75^\circ$<br>$\beta = 73.27^\circ$<br>$\gamma = 96.89^\circ$   | at 66.9 at.% Al, [1993Kat]  |
| $\epsilon$<br>1232-1102                    | <i>cI16?</i><br>-   | $a = 598.0$  | at 61 at.% Al, [1993Kat]  |
| FeAl<br>< 1310                             | <i>cP2</i><br><i>Pm<math>\bar{3}m</math></i><br>CsCl                      | $a = 289.48$ to $290.5$<br>$a = 289.53$ to $290.9$<br>$a = 289.81$ to $291.01$<br>$a = 289.76$ to $190.78$   | 34.5 - 47.5 at.% Al, [1961Lih]<br>36.2 - 50.0 at.% Al, [1958Tay]<br>39.7 - 50.9 at.% Al, [1997Kog] 500°C<br>quenched in water<br>room temperature |
| Fe <sub>3</sub> Al<br>< 547                | <i>cF16</i><br><i>Fm<math>\bar{3}m</math></i><br>BiF <sub>3</sub>         | $a = 579.30$ to $578.86$<br>$a = 579.30$ to $578.92$   | ~24~37 at.% Al, [2001Ike]<br>23.1-35.0 at.% Al, [1958Tay]<br>24.7 - 31.7 at.% Al, [1961Lih]   |
| Fe <sub>2</sub> Al <sub>9</sub>            | <i>mP22</i><br><i>P2<sub>1</sub>/c</i><br>Co <sub>2</sub> Al <sub>9</sub> | $a = 869$<br>$b = 635$<br>$c = 632$<br>$\beta = 93.4^\circ$  | metastable<br>81.8 at.% Al [1993Kat]  |
| FeAl <sub>6</sub>                          | <i>oC28</i><br><i>Cmc2<sub>1</sub></i><br>FeAl <sub>6</sub>               | $a = 744.0$<br>$b = 646.3$<br>$c = 877.0$<br>$a = 744$<br>$b = 649$<br>$c = 879$   | metastable<br>85.7 at.% Al [1993Kat]<br>[1998Ali]   |
| FeAl <sub>4+x</sub>                        | <i>I**</i>  | $a = 884$<br>$c = 2160$  | ( $0 < x < 0.4$ ) metastable<br>[1998Ali]   |

| Phase /<br>Temperature Range<br>[°C]                | Pearson Symbol/<br>Space Group/<br>Prototype                         | Lattice Parameters<br>[pm]  | Comments/References  |
|---|--|---|--|
| $\text{Ce}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$      | <i>hR57</i><br><i>R<math>\bar{3}m</math></i>                         |   | $0 \leq x \leq 0.67$   |
| $\text{Ce}_2\text{Fe}_{17}$                         | $\text{Th}_2\text{Zn}_{17}$  | $a = 851.2$<br>$c = 1245$<br>$a = 855.5$<br>$c = 1249.5$<br>$a = 899.8$<br>$c = 1297$ | $x = 0$ [1969Zar]<br>$x = 0.1$ [1998Kuc]<br>$x = 0.67$ [1969Zar] |
| $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$           | <i>cF24</i><br><i>Fd<math>\bar{3}m</math></i>                        | $a = 734 \pm 2$   | $0 \leq x \leq 0.125$<br>[1985Fra] $x = 0.125$                   |
| $\text{CeFe}_e$                                     | $\text{MgCu}_2$  | $a = 730.4$   | [V-C]  |
| $\alpha\text{Ce}_3\text{Al}_{11}$<br>< 1020         | <i>oI28</i><br><i>Immm</i><br>$\alpha\text{Al}_{11}\text{La}_3$      | $a = 439.5$<br>$b = 1302.$<br>$c = 1009$  | [1988Gsc]  |
| $\beta\text{Ce}_3\text{Al}_{11}$<br>1235-1020       | <i>tI10</i><br><i>I4/mmm</i><br>$\text{Al}_4\text{Ba}$               | $a = 437.7$<br>$c = 1008$   | [1988Gsc]  |
| $\text{CeAl}_3$<br>< 1135                           | <i>hP8</i><br><i>P6<math>_3</math>/mmc</i><br>$\text{Ni}_3\text{Sn}$ | $a = 654.7$<br>$c = 461.0$  | [1988Gsc]  |
| $\text{CeAl}_2$<br>< 1480                           | <i>cF24</i><br><i>Fm<math>\bar{3}m</math></i><br>$\text{MgCu}_2$     | $a = 806.1$   | [1988Gsc]  |
| $\text{CeAl}$<br>< 845                              | <i>oC16</i><br><i>Cmc2</i> or <i>Cmcm</i><br>$\text{CeAl}$           | $a = 926.9$<br>$b = 768.0$<br>$c = 576.1$   | [1988Gsc]  |
| $\beta\text{Ce}_3\text{Al}$                         | <i>CP4</i><br><i>Pm<math>\bar{3}m</math></i><br>$\text{AuCu}_3$      | $a = 498.9$   | [1988Gsc]  |
| $\alpha\text{Ce}_3\text{Al}$                        | <i>hP8</i><br><i>P6<math>_3</math>/mmc</i><br>$\text{Ni}_3\text{Sn}$ | $a = 704.2$<br>$c = 545.1$  | [1988Gsc]  |
| * $\tau_1$ , $\text{CeFe}_4\text{Al}_8$             | <i>tI26</i><br><i>I4/mmm</i><br>$\text{ThMn}_{12}$                   | $a = 886$<br>$c = 508$<br>$a = 880.5$<br>$c = 504.8$                                  | [1961Gla]<br>[1976Bus]   |
| * $\tau_2$ , $\text{CeFe}_2\text{Al}_{10}$          | <i>oC52</i><br><i>Cmcm</i><br>$\text{YbFe}_2\text{Al}_{10}$          | $a = 900.02$<br>$b = 1022.2$<br>$c = 907.3$   | [1998Thi]  |
| * $\tau_3$ , $\text{Ce}_6\text{Fe}_{11}\text{Al}_3$ |  | $a = 819.03$<br>$c = 2310.08$   | [1992Hu]   |
| * $\tau_4$ , $\text{CeFe}_2\text{Al}_8$             | <i>oP44</i><br><br>$\text{CeFe}_2\text{Al}_8$                        | $a = 1251$<br>$b = 1448$<br>$c = 407$   | [1974Yar]  |



| Phase /<br>Temperature Range<br>[°C]                           | Pearson Symbol/<br>Space Group/<br>Prototype | Lattice Parameters<br>[pm]            | Comments/References   |
|--|--|---------------------------------------|---|
| * $\tau_5$ , $\text{CeFe}_2\text{Al}_7$                        | ?  | ?                                     | [1969Zar]<br>perhaps $\text{CeFe}_2\text{Al}_8$                                   |
| * $\tau_6$ , $\text{CeFe}_{1-1.4}\text{Al}_{1-0.6}$            | ?  | ?                                     | [1969Zar],<br>not found and refused by [1976Bus]                                  |
| * $\tau_7$ , $\text{CeFeAl}$                                   | orthorh.                                     | $a = 1020$<br>$b = 1620$<br>$c = 420$ | metastable [1986Ang],<br>sample containing 7 to 9 mass% Fe and<br>3 to 7 mass% Ce |
| * $\tau_8$ , $\text{Ce}_{7.4}\text{Fe}_{27.4}\text{Al}_{65.2}$ | ?  | ?                                     | metastable [1987Yan]  |
| * $\tau_9$ , $\text{CeFe}_5\text{Al}_{20}$                     | ?  | ?                                     | metastable [1988Aye]<br>decagonal quasicrystal                                    |

**Fig. 1: Al-Ce-Fe.**  
Isothermal section at  
500°C, after  
[1969Zar] (revised)



**Fig. 2: Al-Ce-Fe.**

Isopleth along  
 $\text{CeFe}_2\text{Al}_{10}$  - Al  
 (partially), after  
 [1988Sok]

