Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Redetermination of the lanthanum iron sulfide $La_{52}Fe_{12}S_{90}$

Allison M. Mills, Daniel Bräunling and Michael Ruck*

Institut für Anorganische Chemie, Technische Universität Dresden, D-01062 Dresden, Germany
Correspondence e-mail: michael.ruck@chemie.tu-dresden.de

Received 13 December 2005
Accepted 24 April 2006

A redetermination of the structure of '$La_{32.66}Fe_{11}S_{60}$' in the trigonal space group $R\overline{3}m$ led to the new formula $La_{52}Fe_{12}S_{90}$ and to a redefinition of the structure type. In the structure, the Fe^{2+} cations occur in Fe_2S_9 dimers of face-sharing octahedra (with $3m$ symmetry). The dimers are linked by face- and vertex-sharing bi- and tricapped LaS_6 trigonal prisms (with m symmetry) to form a three-dimensional network containing two types of cuboctahedral cavities. The larger cavities remain empty, while the smaller ones accommodate alternative sites for disordered La^{3+} cations.

Comment

In a search for materials with interesting magnetic properties, we have begun a reinvestigation of the R–Fe–S system (R = rare earth metal). With the larger rare-earth metals, phases of three different compositions are formed, *viz.* $R_2Fe_{2-\delta}S_5$ (R = La, Ce and Pr), $R_3Fe_{2-\delta}S_7$ (R = La, Ce, Pr and Nd) and $R_{52}Fe_{12}S_{90}$ (R = La, Ce, Pr and Nd) (Collin *et al.*, 1968; Patrie *et al.*, 1968; Du & Tang, 1984). We have recently determined the structures of $Ce_2Fe_{1.82}S_5$ (Harms *et al.*, 2005) and $Ce_3Fe_{1.94}S_7$ (Mills & Ruck, 2004). The structure of $La_{52}Fe_{12}S_{90}$ is reported here.

$La_{52}Fe_{12}S_{90}$ adopts a structure type that has been the source of considerable confusion. The existence of a family of compounds of composition R_2TS_4 (R = La and Ce, and T = Cr, Mn and Fe) having monoclinic cell parameters was first reported by Patrie *et al.* (1968). The crystal structures of $La_{32.66}T_{11}S_{60}$ (T = Mn and Fe) were subsequently determined in the non-standard monoclinic space group Bm (Collin & Laruelle, 1974), but it was later suggested that the symmetry of the structures is actually trigonal (Cenzual *et al.*, 1990). More recently, an X-ray diffraction investigation of $La_{15.9}Cr_{5.4}S_{32}$ established that the correct space group for the structure type is $R\overline{3}m$ (Litteer *et al.*, 1999). We report here the redetermination of '$La_{32.66}Fe_{11}S_{60}$' in $R\overline{3}m$ and propose the new formula $La_{52}Fe_{12}S_{90}$. Views of the structure along [001] and [110] are presented in Figs. 1 and 2, and selected geometric parameters are listed in Table 1.

The two independent Fe atoms occur in Fe_2S_9 dimers of face-sharing octahedra, which reside on the $\overline{3}$ axes. The dimers are composed of octahedra that are trigonally compressed along [001]. The terminal Fe1—S3 and Fe2—S1 distances are both shorter than the bridging Fe1—S2 and Fe2—S2 distances (Table 1), suggesting a repulsion between the iron cations. The resulting Fe1···Fe2 distance of 3.222 (7) Å is considerably

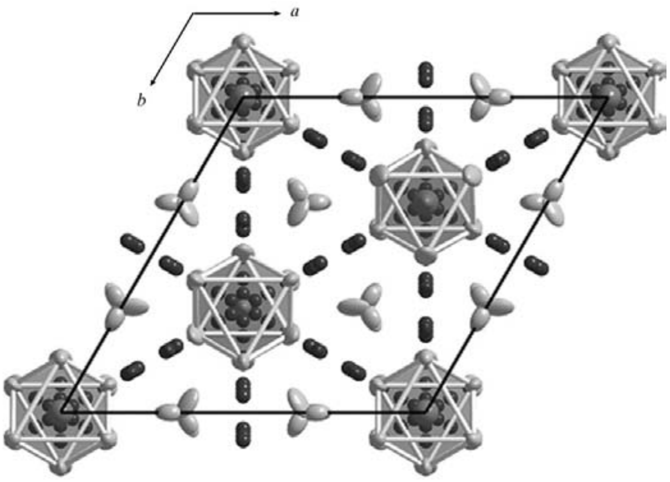

Figure 1
View of the structure of $La_{52}Fe_{12}S_{90}$ along [001]. Displacement ellipsoids are drawn at the 90% probability level. Key: La atoms are dark grey, Fe atoms medium grey and S atoms light grey.

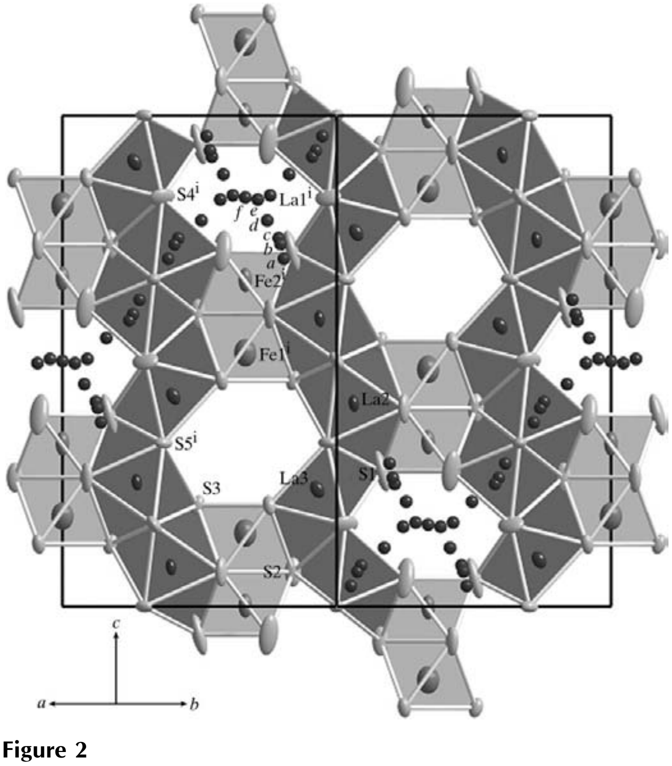

Figure 2
A [110] section of the structure of $La_{52}Fe_{12}S_{90}$, with the atomic labelling scheme indicated. Displacement ellipsoids are drawn at the 90% probability level. Key: La atoms are dark grey, Fe atoms medium grey and S atoms light grey. [Symmetry code: (i) $x + \frac{2}{3}, y + \frac{1}{3}, z + \frac{1}{3}$.]

DOI: 10.1107/S0108270106014879

longer than the 2.980 (6) Å distance between Fe atoms in the $[FeS_{6/2}]$ chains of $Ce_3Fe_{1.94}S_7$ (Mills & Ruck, 2004). The Fe—S distances in $La_{52}Fe_{12}S_{90}$ are comparable to those of 2.45–2.67 Å found in the FeS_6 octahedra of $La_2Fe_2S_5$ (Besrest & Collin, 1977).

The La atoms occupy several different types of coordination environments, owing in part to the positional disorder of atom La1 (see below). The most populated La1 site, La1*b*, and the fully occupied La2 and La3 sites centre bi- and tricapped trigonal prisms (or, alternatively, square antiprisms and monocapped square antiprisms) of S atoms. If all La—S distances less than 4 Å are considered, then La1*b* [La1*b*—S = 2.774 (4)–3.352 (6) Å] and La3 [La3—S = 2.8995 (13)–3.811 (5) Å] can be described as eight-coordinate, and La2 [La2—S = 2.875 (3)–3.437 (4) Å] as nine-coordinate. The range of La—S distances is similar to that observed in the capped trigonal prisms of $La_4Ge_3S_{12}$ (2.86–3.73 Å; Mazurier & Etienne, 1974).

In addition to sharing faces and vertices with one another, the prisms each share either one (La1*b*S_8 and La3S_8) or two (La2S_9) faces with an Fe_2S_9 dimer, as well as a vertex with a neighbouring dimer. The dimers, in turn, share their 12 lateral faces and all of their vertices with La-centred polyhedra. The resulting three-dimensional network contains large cuboctahedral cavities. Two types of cavities alternate along the $\overline{3}$ axes, separated by the Fe_2S_9 dimers. Smaller cavities outlined by six S1 and six S4 atoms surround the 3*b* sites, and larger cavities outlined by six S3 and six S5 atoms surround the 3*a* sites. The volumes of the cavities defined by the atom centres are 114 and 132 $Å^3$, respectively (calculated using the program *VOID95*; Koch & Fischer, 1995).

While the larger cavity remains empty, the smaller cavity accommodates alternative sites for the disordered La atom, La1. Site La1*b*, at the edge of the cavity, is non-ideal, since it is located only 3.60 (2) Å from itself. The La atoms, therefore, move away from this position and occupy a path of six closely spaced sites (La1*a*–La1*f*) that extends into the neighbouring cavity (Fig. 3). The total occupancy of these sites is 8/9, the vacancies being necessary for charge balance. The outer sites, La1*a*–La1*c*, which have a combined occupancy of approximately 80%, are eight-coordinate, with bicapped trigonal–prismatic (or square–antiprismatic) coordination geometries similar to those of La2 and La3. However, more unusual coordination environments are encountered for the inner sites, La1*d*–La1*f*, which have individual occupancies ranging from only 1 to 7%. La1*d* is coordinated by five S atoms in a square–pyramidal arrangement, La1*e* is coordinated by eight S atoms in a bicapped trigonal–prismatic arrangement, and La1*f*, located at the centre of the cavity, is coordinated by six S atoms in an octahedral arrangement. The split La1 positions suggest that the trivalent cations are mobile; the sparsely occupied inner sites can be regarded as local energy minima on the path between the more favourable outer sites.

Aside from symmetry considerations, the main differences between our structural model and those previously proposed for the structure type involve the filling of the two cavities. In the first structures of this type to be determined, $La_{32.66}T_{11}S_{60}$ (T = Mn and Fe), the smaller cavity contains an implausible T_2 dumb-bell, and the sites at the edge of the cavity, equivalent to La1*b* in our structure, are 60–80% occupied (Collin & Laruelle, 1974). In the more recently published structure of $La_{15.9}Cr_{5.4}S_{32}$, three sites just outside the smaller cavity are partially filled by La or Cr, with a total occupancy of approximately 90%, and one site inside the cavity is occupied by an S atom with a non-positive definite displacement ellipsoid (Litteer *et al.*, 1999). An additional S atom is located inside the larger cavity, which remains empty in the other structures. However, since $La_{15.9}Cr_{5.4}S_{32}$ was synthesized in an $LaCl_3$ flux, it is possible that this site actually belongs to a misassigned Cl atom. Using a similar synthetic method, we have recently isolated the compounds $Ce_{53}Fe_{12}S_{90}X_3$, in which X atoms (X = Cl, Br or I) occupy this site, from reactions in CeX_3 fluxes. The structures of the filled compounds will be communicated shortly (Mills & Ruck, 2006).

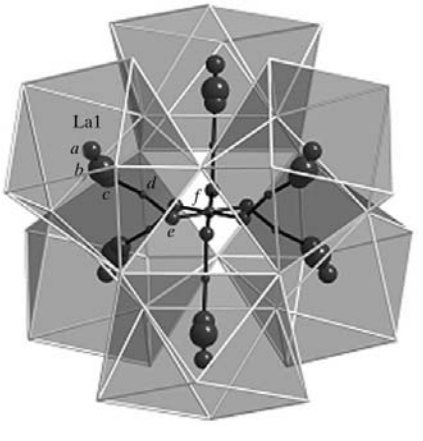

Figure 3
Positional disorder of La1 in $La_{52}Fe_{12}S_{90}$. A path of six closely spaced sites extends into the smaller cuboctahedral cavity. The size of the La1*a*–La1*f* atoms at each site represents their occupancy, and the lines connecting them represent possible paths between the sites. The total occupancy of the sites is 8/9.

Experimental

Hexagonal prisms of $La_{52}Fe_{12}S_{90}$ were unexpectedly isolated from a flux reaction designed to produce $La_3Fe_2S_7$. The starting reactants were lanthanum (rod, > 99.5%, Treibacher; freshly filed under argon prior to use), iron (powder, 99.99%, ABCR) and sulfur [powder, > 99%, VEB Laborchemie; recrystallized from CS_2, then purified of carbon according to the method of von Wartenberg *et al.* (1956)]. A 1:1 mixture of LiCl (p.a., Merck) and KCl (p.a., J. T. Baker) was used as a flux after being heated under dynamic vacuum to remove any moisture. The elements, in an La:Fe:S ratio of 3:2:7 (0.25 g in total), were added to the LiCl/KCl flux (0.5 g) in a fused-silica ampoule (6 cm in length and 0.8 cm in diameter), which was then sealed under vacuum (10^{-3} Torr). The reaction mixture was heated at 1170 K for four days and then cooled to room temperature over a period of four days. The flux was removed by washing the sample several times with water and ethanol. Energy-dispersive X-ray (EDX) analysis on a Philips XL30 scanning electron microscope of crystals isolated from the product confirmed the presence of La, Fe and S in the appropriate ratios. Analysis (mol%): La 34.8 (2), Fe 7.1 (5), S 58.1 (3) (average of two analyses).

Crystal data

$La_{52}Fe_{12}S_{90}$
$M_r = 10778.92$
Trigonal, $R\overline{3}m$
$a = 14.0426$ (5) Å
$c = 21.776$ (1) Å
$V = 3718.8$ (3) Å^3
$Z = 1$
$D_x = 4.813$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 16.96$ mm^{-1}
$T = 293$ (2) K
Prism, black
0.15 × 0.12 × 0.10 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: numerical [*X-RED* (Stoe & Cie, 2001); crystal description optimized based on equivalent reflections using *X-SHAPE* (Stoe & Cie, 1999)]
$T_{\min} = 0.210$, $T_{\max} = 0.363$
19622 measured reflections
1018 independent reflections
1000 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 27.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.104$
$S = 1.20$
1018 reflections
65 parameters
$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 405P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 3.27$ e Å^{-3}
$\Delta\rho_{\min} = -4.12$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00033 (2)

Table 1
Selected bond lengths (Å).

La1*b*—S1$^{\rm ii}$	2.774 (4)	La2—S4$^{\rm ix}$	3.437 (4)
La1*b*—S2$^{\rm iii}$	2.858 (7)	La3—S3$^{\rm ix}$	2.8995 (13)
La1*b*—S4$^{\rm iv}$	3.022 (6)	La3—S4$^{\rm x}$	2.9132 (6)
La1*b*—S2$^{\rm v}$	3.249 (9)	La3—S1	2.968 (5)
La1*b*—S5$^{\rm vi}$	3.352 (6)	La3—S5$^{\rm iii}$	2.9769 (19)
La2—S3$^{\rm vii}$	2.875 (3)	La3—S2	3.811 (5)
La2—S2$^{\rm iii}$	2.9006 (10)	Fe1—S3$^{\rm vi}$	2.456 (4)
La2—S5$^{\rm iii}$	2.9737 (5)	Fe1—S2$^{\rm vi}$	2.727 (6)
La2—S3$^{\rm viii}$	2.983 (4)	Fe2—S1$^{\rm ii}$	2.432 (6)
La2—S1	3.247 (8)	Fe2—S2$^{\rm vi}$	2.595 (5)

Symmetry codes: (ii) $-x + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{2}{3}$; (iii) $-y + \frac{2}{3}, x - y + \frac{1}{3}, z + \frac{1}{3}$; (iv) $-y, x - y, z$; (v) $y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$; (vi) $-x + \frac{2}{3}, -y + \frac{1}{3}, -z + \frac{1}{3}$; (vii) $-x + \frac{4}{3}, -y + \frac{2}{3}, -z + \frac{2}{3}$; (viii) $x - \frac{1}{3}, y + \frac{1}{3}, z + \frac{1}{3}$; (ix) $-x + y + 1, -x + 1, z$; (x) $y + \frac{1}{3}, -x + y + \frac{2}{3}, -z + \frac{2}{3}$.

In the new data set collected for the title compound, the intensity statistics were consistent with Laue symmetry $\overline{3}m$, and a trigonal cell was found. The only systematic reflection condition obeyed was that for *R*-centring (*hkl*: $-h + k + l = 3n$, obverse setting). The centrosymmetric space group $R\overline{3}m$ was therefore chosen on the basis of the close relationship between the structures of $La_{52}Fe_{12}S_{90}$ and $La_{15.9}Cr_{5.4}S_{32}$ (Litteer *et al.*, 1999). No evidence of superstructure, symmetry lowering or twinning was observed. After three lanthanum, two iron and five sulfur sites had been found through repeated refinements and difference Fourier syntheses, additional residual electron density remained in a series of closely spaced sites extending from La1 to the centre of the neighbouring cuboctahedral cavity at $(0, 0, \frac{1}{2})$. These were attributed to a positional disorder of La1. The six split positions La1*a*–La1*f* were refined with the same isotropic displacement parameter, and their occupancies were constrained to total 8/9, as required for charge balance. The occasional filling of the cavity requires a structural readjustment, which is reflected in the larger displacement ellipsoids of some atoms, particularly those defining the cavity (S1 and S4). Atomic positions were standardized using the program *STRUCTURE TIDY* (Gelato & Parthé, 1987).

Data collection: *X-AREA* (Stoe & Cie, 2004); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

The authors gratefully acknowledge the experimental help of Ms Jutta Krug and the financial support of the Deutsche Forschungsgemeinschaft (DFG) within the SFB 463.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1068). Services for accessing these data are described at the back of the journal.

References

Besrest, F. & Collin, G. (1977). *J. Solid State Chem.* **21**, 161–170.
Brandenburg, K. (1999). *DIAMOND*. Version 2.1c. Crystal Impact, Bonn, Germany.
Cenzual, K., Gelato, L. M., Penzo, M. & Parthé, E. (1990). *Z. Kristallogr.* **193**, 217–242.
Collin, G. & Laruelle, P. (1974). *Acta Cryst.* B**30**, 1134–1139.
Collin, G., Rouyer, F. & Loriers, J. (1968). *C. R. Acad. Sci. Ser. C*, **266**, 689–691.
Du, Y. & Tang, G. (1984). *Huaxue Tongbao*, **2**, 18–19.
Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.
Harms, W., Mills, A. M., Söhnel, T., Laubschat, C., Wagner, F. E., Geibel, C., Hossain, Z. & Ruck, M. (2005). *Solid State Sci.* **7**, 59–66.
Koch, E. & Fischer, W. (1995). *VOID95*. Philipps-Universität Marburg, Germany.
Litteer, J. B., Sirchio, S. A., Fettinger, J. C., Smolyaninova, V., Eichhorn, B. W. & Greene, R. L. (1999). *Chem. Mater.* **11**, 1179–1182.
Mazurier, A. & Etienne, J. (1974). *Acta Cryst.* B**30**, 759–762.
Mills, A. M. & Ruck, M. (2004). *Acta Cryst.* C**60**, i71–i72.
Mills, A. M. & Ruck, M. (2006). *Inorg. Chem.* In the press.
Patrie, M., Nguyen, H.-D. & Flahaut, J. (1968). *C. R. Acad. Sci. Ser. C*, **266**, 1575–1578.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (1999). *X-SHAPE*. Version 1.06. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (2001). *X-RED*. Version 1.22. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (2004). *X-AREA*. Version 1.25. Stoe & Cie, Darmstadt, Germany.
Wartenberg, H. von (1956). *Z. Anorg. Allg. Chem.* **286**, 243–246.