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Crystal Structure Refinements of the B 20 and Monoclinic (CoGe-type) Polymorphs of FeGe

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The crystal structures of the B 20 and monoclinic polymorphs of FeGe have been refined from single-crystal X-ray diffraction data. Above about 620°C the B 20 form transforms to the previously described B 35 (CoSn-type) modification and this in turn undergoes a transition at 740°C to the high-temperature monoclinic polymorph isostructural with CoGe. Cell parameters for the monoclinic (space group $C2/m$) phase are: $a = 11.838 \pm 0.001$ Å, $b = 3.9371 \pm 0.0004$ Å, $c = 4.9336 \pm 0.0004$ Å, and $\beta = 103.514 \pm 0.007°$. The cubic unit cell of the B 20 form has the dimension $a = 4.700 \pm 0.002$ Å. Atomic parameters are reported and the coordinations and other crystal-chemical properties of the three FeGe polymorphs are discussed and compared.

Phases occurring in the Fe-Ge system have been the subject of an active interest in recent years, especially on account of the magnetically ordered structures that they often possess. A recent paper by Adelson and Austin[1] should be consulted as an example of a study on the magnetic ordering in the $Fe_{(2-x)}Ge$ ($B8_2$) and $FeGe_2$ (C 16) phases by means of neutron diffraction, and for some further references pertinent to this type of investigation. The composition region between the Ge-rich boundary of the $B8_2$ ($Fe_{(2-x)}Ge$) field and the phase $FeGe_2$ has been studied in the current investigation. Of the phases occurring in this region, the B 35 modification of FeGe has been previously described by Ohoyama *et al.*[2] and subsequently confirmed by other authors. The K (kappa) phase found by Kanematsu and Ohoyama[3] and also previously by Olofsson[4] was also found in the present study, but has not yet been characterised. Several details concerning the ordering in the Ge-rich modification of the $B8_2$ phase would seem to require further clarification, and are the subject of a structural investigation now in progress. These three phases, together with the two new FeGe polymorphs described in this paper, have been found in the current investigations. Phase relations between the compounds occurring in this region, as well as a description of preparative methods based on halogen-transport reactions are to be found in a separate paper,[5] and will consequently be only superficially mentioned in the following.

PREPARATION AND CELL DIMENSIONS

Crystals of the B 20 iron monogermanide were grown from an iodine-containing gas phase at 450°C, and crystals of the monoclinic polymorph were grown at 742°C by a similar chemical transport reaction using bromine as carrier. Cell dimensions were obtained from powder photographs taken at 20 ± 2°C in Guinier-Hägg focussing cameras using Cr$K\alpha_1$ radiation ($\lambda = 2.28962$ Å) and with silicon as internal reference standard ($a = 5.4305$ Å). There are no indications that the cell dimensions of these phases vary significantly with the method of preparation.[5] A least-squares program CELSIUS [13] was used to refine cell dimensions for a specimen of the monoclinic phase obtained by heating an FeGe alloy at 740°C. The monoclinic unit cell had dimensions:

$$\begin{aligned} a &= 11.838 \pm 0.001 \text{ Å} \\ b &= 3.9371 \pm 0.0004 \text{ Å} \\ c &= 4.9336 \pm 0.0004 \text{ Å} \\ \beta &= 103.514 \pm 0.007^\circ \end{aligned}$$

for this specimen (19 reflections). The standard deviations are those calculated by the program, and do not take into account possible systematic errors. The cubic unit cell was found to have the dimension $a = 4.700 \pm 0.002$ Å.

REFINEMENT OF B 20 STRUCTURE

A well-formed crystal of approximately tetrahedral shape and a maximum dimension of about 0.08 mm was selected for the structure refinement. Weissenberg photographs taken with Zr-filtered Mo$K\alpha$ radiation were used to record intensity data for 94 independent $hk0$ reflections using the multiple-film technique with four films interleaved with thin iron foils. A calibrated intensity scale was obtained from one of the reflections of the crystal and used for the visual estimation of intensities. These were corrected for Lorentz and polarisation effects [14] to obtain a set of structural amplitudes. The crystal was lost through a mishap before it could be measured for an absorption correction. An application of such a correction would have improved the accuracy of the data since the linear absorption coefficient is quite high for this compound ($\mu_{\text{Mo}K\alpha} = 438$ cm^{-1}). On the basis of the probable space group ($P2_13$) and the cell dimension the assumption was made that the structure was of the B 20 type, and this hypothesis was confirmed by a calculation of structure factors [15] using the atomic parameters reported for FeSi.[6] After the observed structural amplitudes had been placed on an absolute scale, they showed good agreement with the calculated structure factors. A Fourier summation of the electron density projected on the basal plane was then made [16] using the calculated phase angles. This enabled more accurate values for the atomic parameters to be obtained, and these were used for a further electron-density calculation. A graphical plot of $\log|F_c|/|F_o|$ against $\sin^2\theta$ was used to obtain an approximate overall temperature factor, and from this graph it was evident that some strong reflections at low angles showed considerable extinction effects. In the last refinement made by Fourier methods the structure factors for seven of these reflections were set equal to the calculated values from the previous cycle. This did not produce significant changes in the positional parameters, wheras the discrepancy index $R = \sum||F_o - F_c||/\sum|F_o|$ was reduced from 0.16 to 0.10. A full-matrix least-squares refinement of the two positional parameters, two isotropic temperature factors and one scale factor was then carried out using the program LALS.[17] A weighting scheme according to Cruickshank *et al.*,[18] $w = 1/(a + |F_o| + c|F_o^2|)$, was used where the constants a and c were given the values 10 and 0.048, respectively. The atomic scattering factors, including corrections for the real and complex parts of the anomalous dispersion, were taken from *International Tables*.[19] Reflections too weak to be observed, together with the seven showing extinction effects were omitted from the refinement, and are not included in the calculation of the R-value. Three refinement cycles were carried out, the final shifts in the parameters being not greater than 0.2 % of the standard deviations. The results of the structural refinement are summarised in Table 1.

Table 1. The structure of low-temperature FeGe (FeSi-type).

Space-group: $P2_13$ (T^4), No. 198, $Z = 4$.
$a = 4.700 \pm 0.002$ Å, $U = 103.8$ Å^3, $\varrho_x = 8.22$ g·cm^{-3}

Atom	Position	x	$\sigma(x)$	Isotropic temperature factor B	$\sigma(B)$
Fe	4(a)	0.1352	0.0004	0.06	0.03
Ge	4(a)	0.8414	0.0003	0.13	0.03

Final R value = 0.097

Interatomic distances less than 3 Å:

	distance (Å)	standard deviation
Fe – Ge	2.391	0.004
– 3 Ge	2.443	0.002
– 3 Ge	2.646	0.003
– 6 Fe	2.881	0.001
Ge – Fe	2.391	0.004
– 3 Fe	2.443	0.002
– 3 Fe	2.646	0.003
– 6 Ge	2.912	0.001

REFINEMENT OF MONOCLINIC STRUCTURE (CoGe-TYPE)

Well-faceted crystals of monoclinic FeGe were grown from the vapour phase in a halogen-transport experiment.[5] The growth habit was prismatic about the b-axis and crystals were elongated in this crystallographic direction. Frequent examples of twinning on the (100) plane were encountered, the twins being further related by a rotation of 180° about a mutual c-axis. The monocrystalline fragment used for collecting intensity data was cut from a larger crystal. Weissenberg photographs were used in the same way as described above to estimate intensities for 157 independent $h0l$ reflections. All the bounding planes of the fragment were crystallographic growth faces except for the two surfaces produced by cutting, and the crystal could be accurately measured for an absorption correction of the data. This correction, together with that for Lorentz and polarisation effects was made using the program DATAP-2.[20] Systematic extinctions were only observed for reflections of the type hkl when the sum $(h + k)$ was odd, indicating that the possible space-groups are Cm or $C2/m$.

The space group of CoGe is $C2/m$ [7] and the similarity of the lattice dimensions further suggests isomorphism with the monoclinic form of FeGe. Some preliminary calculations were not in agreement with this hypothesis, but later work showed this to be due to an error and confirmed that CoGe and monoclinic FeGe have the same structure. Initial values for atomic parameters were obtained by Fourier methods assuming the structure determined previously for CoGe.[7] The program LALS [17] was used for a full-matrix least-squares refinement of the scale factor, six atomic parameters and five isotropic temperature factors. Weighting was by the formula suggested by Cruickshank *et al.*,[18] using the values $A = 20$ and $C = 0.013$. Scattering factors corrected for the real part of the anomalous dispersion were obtained from Ref. 19. Reflections too weak to observe were given zero weight, and in the last refinement cycle 6 reflections affected by extinction were removed and are not included in the final R-value. After five least-squares cycles the shifts were less than 0.01 % of the standard deviations, and the R-value was 0.11. A similar refinement was made for the data before absorption corrections had been applied, and including the reflections effected by extinction. An R-value of 0.14 was obtained and the standard deviations of atomic parameters were about 50 % larger. The atomic coordinates differed by less than the standard deviations. Applying absorption corrections to the data had nevertheless

Table 2. Interatomic distances less than 3 Å in the B 35 polymorph of FeGe. (Included for comparison.)

$a = 5.002$ Å, $c = 4.055$ Å.

		distance (Å)
Fe 3(*f*)	— 4 Fe 3 (*f*)	2.501
	— 4 Fe 2 (*d*)	2.489
	— 2 Ge 1 (*a*)	2.501
Ge 2(*d*)	— 6 Fe 3 (*f*)	2.489
	— 3 Ge 2 (*d*)	2.888
Ge 1(*a*)	— 6 Fe 3 (*f*)	2.501

Table 3. Structure of monoclinic FeGe.

Space-Group: $C2/m$ (C_{2h}^3) No. 12. $Z = 8$.
Structure type: CoGe.

$U = 223.6$ Å^3, $\varrho_x = 7.63$ gcm^{-3}
$a = 11.838 \pm 0.001$ Å
$b = 3.9371 \pm 0.0004$ Å
$c = 4.9336 \pm 0.0004$ Å
$\beta = 103.514 \pm 0.007°$

Parameters of atoms in the asymmetric unit ($y = 0$).

						Isotropic temperature factor	
Atom	Position	x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
$\mathrm{Fe_I}$	2(*a*)	0		0		0.27	0.06
$\mathrm{Fe_{II}}$	2(*c*)	0		0.5		0.31	0.06
$\mathrm{Fe_{III}}$	4(*i*)	0.2057	0.0003	0.3576	0.0008	0.39	0.05
$\mathrm{Ge_I}$	4(*i*)	0.8137	0.0002	0.1551	0.0006	0.34	0.04
$\mathrm{Ge_{II}}$	4(*i*)	0.5693	0.0003	0.2979	0.0007	0.56	0.04

a considerable effect on the isotropic temperature factors, which all showed an increase of about 0.2 Å^2 in the value of the constant B. Results of the refinement using absorption-corrected data are given in Table 3. Interatomic distances less than 3.5 Å are given in Table 4, and were calculated using the program DISTAN.[21] Standard deviations were calculated taking into account errors in atomic coordinates and cell dimensions.

DISCUSSION

In the absence of a mineralising agent such as iodine, the polymorphic transformation B 35—B 20 occurs extremely slowly,[5] and this is probably the reason why this phase has not been reported in the literature previously. The very narrow temperature range of about 10°C within which the monoclinic phase is stable means that this polymorph will not be formed except

Table 4. Interatomic distances less than 3.5 Å in the monoclinic (CoGe-type) polymorph of FeGe.

					distance (Å)	σ
$\mathrm{Fe_{I}}$	2(*a*)	— 2	$\mathrm{Fe_{II}}$	2(*c*)	2.467	0.000
		— 4	$\mathrm{Ge_{II}}$	4(*i*)	2.479	0.002
		— 2	$\mathrm{Ge_{I}}$	4(*i*)	2.497	0.003
		— 2	$\mathrm{Fe_{III}}$	4(*i*)	2.652	0.004
$\mathrm{Fe_{II}}$	2(*c*)	— 4	$\mathrm{Ge_{II}}$	4(*i*)	2.434	0.002
		— 2	$\mathrm{Ge_{I}}$	4(*i*)	2.450	0.003
		— 2	$\mathrm{Fe_{I}}$	2(*a*)	2.467	0.000
		— 2	$\mathrm{Fe_{III}}$	4(*i*)	2.687	0.004
$\mathrm{Fe_{III}}$	4(*i*)	—	$\mathrm{Ge_{I}}$	4(*i*)	2.468	0.005
		—	$\mathrm{Ge_{I}}$	4(*i*)	2.486	0.005
		— 2	$\mathrm{Fe_{III}}$	4(*i*)	2.502	0.005
		— 2	$\mathrm{Ge_{II}}$	4(*i*)	2.519	0.003
		—	$\mathrm{Fe_{I}}$	2(*a*)	2.652	0.004
		— 2	$\mathrm{Ge_{I}}$	4(*i*)	2.666	0.003
		—	$\mathrm{Fe_{II}}$	2(*c*)	2.687	0.004
		—	$\mathrm{Ge_{II}}$	4(*i*)	2.805	0.005
$\mathrm{Ge_{I}}$	4(*i*)	—	$\mathrm{Fe_{II}}$	2(*c*)	2.450	0.003
		—	$\mathrm{Fe_{III}}$	4(*i*)	2.468	0.005
		—	$\mathrm{Fe_{III}}$	4(*i*)	2.486	0.005
		—	$\mathrm{Fe_{I}}$	2(*a*)	2.497	0.003
		— 2	$\mathrm{Fe_{III}}$	4(*i*)	2.666	0.003
		— 2	$\mathrm{Ge_{I}}$	4(*i*)	2.723	0.004
		—	$\mathrm{Ge_{II}}$	4(*i*)	3.134	0.004
		— 2	$\mathrm{Ge_{II}}$	4(*i*)	3.366	0.003
		— 2	$\mathrm{Ge_{II}}$	4(*i*)	3.498	0.004
$\mathrm{Ge_{II}}$	4(*i*)	— 2	$\mathrm{Fe_{II}}$	2(*c*)	2.434	0.002
		— 2	$\mathrm{Fe_{I}}$	2(*a*)	2.479	0.002
		— 2	$\mathrm{Fe_{III}}$	4(*i*)	2.519	0.003
		—	$\mathrm{Fe_{III}}$	4(*i*)	2.805	0.005
		—	$\mathrm{Ge_{II}}$	4(*i*)	2.863	0.006
		—	$\mathrm{Ge_{II}}$	4(*i*)	3.013	0.006
		—	$\mathrm{Ge_{I}}$	4(*i*)	3.134	0.004
		— 2	$\mathrm{Ge_{I}}$	4(*i*)	3.366	0.003
		— 2	$\mathrm{Ge_{I}}$	4(*i*)	3.498	0.004

under very well-defined conditions of heat treatment. Polymorphism in alloy phases is of especial interest since it provides a touchstone against which theories of the bonding in these compounds can be critically tested.

An interesting feature of the B 20 structure is the seven-fold coordination of both the metal (M) and the non-metal (A) atoms. These are situated in two sets of 4(i) positions and consequently have one free atomic coordinate (x_m and x_a). It is possible to define an "ideal" B 20 structure in which these parameters are related according to:

$$x_m = -x_a = (\sqrt{5}-1)/8 = 0.155$$

and this leads to some especially simple geometrical relationships which will be discussed further. Schob and Parthé [8] have pointed out that the B 20 structure then has commutative partial structures, *viz.* an interchange of the atoms produces an identical structure. These authors also point out that the radius ratios of the atoms in known representatives of this structure type fall within a much smaller range of values than that dictated by the space-filling principle [9] for the existence of M—A contacts. The seven nearest neighbours of the other kind are at two sets of three symmetry-equivalent distances, and one other distance. In the ideal structure these seven distances are identical, and are related to the unit cell dimension by:

$$d_7 = a(\sqrt{15}-\sqrt{3})/4 = 0.535a$$

There is also a set of six neighbours of the same kind situated more remotely at a symmetry-equivalent distance of:

$$d_6 = a(\sqrt{3-\sqrt{5}})/2 = 0.618a$$

It is interesting to see to what extent the ideal interatomic distance d_7 in the B 20 structure correlates with a radius sum appropriate to sevenfold coordination (using a conversion factor $r'_7 = 0.968\ r_{12}$, obtained from the graph of the decrease in metallic coordination radius *vs.* coordination number [10]). On calculating the values of d_7 from the cubic cell dimensions of binary B 20 phases listed in Ref. 8 it is found that the values of this parameter are consistently lower than the radius sums corrected for sevenfold coordination. This contraction is lowest for AuBe (0.0 %) and greatest for PtMg (9.7 %), and has an average value of about 3 %. A systematic trend in the contraction can be noted in the series CrSi (2.3 %), MnSi (4.7 %), FeSi (5.1 %), and CoSi (5.6 %), and this may be indicative of a stronger binding between metal and non-metal atoms with increasing electron concentration. The same trend in the contraction can be noted within the pairs RuSi (1.9 %), RhSi (3.4 %), and CrGe (0.8 %), FeGe (2.3 %). Refinements of the atomic parameters in B 20 structures have been made for CrSi, MnSi, CoSi,[11] FeSi,[6] RhSi,[12] and FeGe (this work). Values of x_A close to the ideal value 0.845 have been found for all of these compounds, whilst in all cases the metal atom parameter is smaller than the ideal value $x_M = 0.155$.

This decrease in the value of x_M serves to diminish the distance between the metal atom and its nearest metal neighbours. Iron germanide shows the smallest value of x_M within the group of B 20 structures for which atomic parameter values are available, but the deviation is nevertheless not sufficient

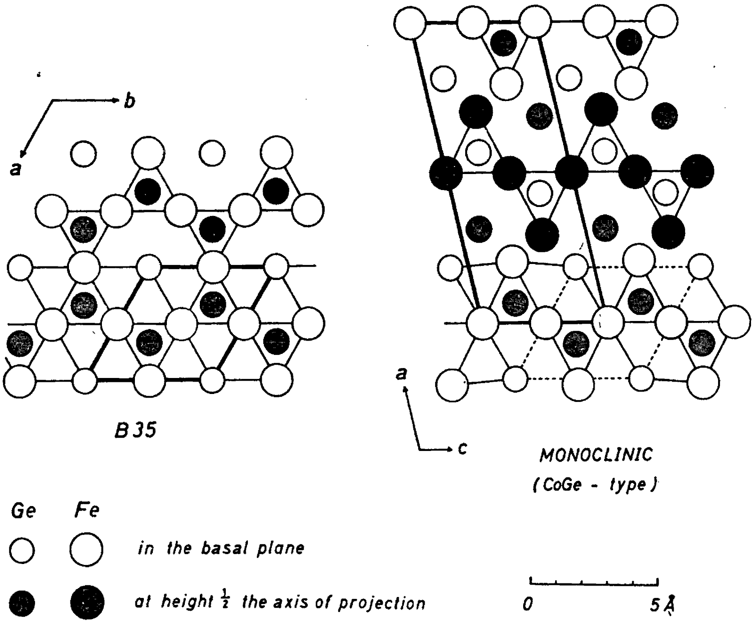

Fig. 1. Structural projections of the B 35 and monoclinic (CoGe-type) polymorphs of FeGe. The distorted sub-unit of the monoclinic structure corresponding to the B 35 unit cell is shown with dotted lines.

to bring nearest iron atoms closer than a distance which exceeds the Goldschmidt diameter for 12-coordination by 13 %. On the other hand, the Ge—Ge distances exceed the 12-coordination metallic diameter by only 5 %, and there is therefore some justification for assigning a 13-fold coordination to the non-metal atoms in FeGe. A rather efficient packing in the B 20 phase is indicated by the high value of 8.22 g·cm^{-3} for the X-ray density, compared with the values 7.28 and 7.63 for the B 35 and monoclinic polymorphs, respectively. Some structural features of the latter two phases can be seen in Fig. 1. A sub-unit of the monoclinic structure corresponding to a slight distortion of the hexagonal unit cell of the B 35 phase is indicated with dotted lines. This sub-unit repeats by translation in the *b*- and *c*-directions, whereas the repetition is without limit in all three axial directions for the B 35 structure. Consequently, the triangular prismatic coordination of the 2(*d*) Ge atoms in the latter structure is quite similar to the coordination of Ge_{II} in the monoclinic phase, whilst the coordination of the iron atoms in the B 35 structure corresponds to the coordination of Fe_I and Fe_{II} in the high temperature polymorph.

The planar coordination of the 1(*a*) Ge atom in the B 35 structure by six iron atoms is replaced in the monoclinic phase by a less-regular coordination shell with six iron atoms and two germanium atoms. There is no counterpart in the B 35 structure to the coordination of the iron atom (Fe_{III}) in the 4(*i*) position of the monoclinic polymorph.

The Fe—Fe contacts between Fe_I 2(*a*) and Fe_{II} 2(*c*) in the monoclinic form are rather short (2.467 Å) for a phase that is not rich in iron. A comparison may be made with the corresponding distance of 2.501 Å in the B 35 phase, and the other Fe—Fe contact of 2.652 Å in the monoclinic polymorph.

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