Structural investigations of $\varepsilon$-FeGe at high pressure and low temperature

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Abstract

The structural parameters of $\varepsilon$-FeGe have been determined at ambient conditions using single crystal refinement. Powder diffraction has been carried out to determine structural properties and compressibility for pressures up to 30 GPa and temperatures as low as 82 K. The discontinuous change in the pressure dependence of the shortest Fe–Ge interatomic distance might be interpreted as a symmetry-conserving transition and seems to be related to a magnetic phase boundary line.

Keywords: Structural refinement; High pressure; Low temperature; Compressibility

1. Introduction

Binary transition metal compounds crystallizing in the $B20$ structure (space group $P2_13$) [1,2] show a variety of interesting physical properties ranging from a narrow-gapped semiconductor (FeSi) to diamagnetic (CoSi) or paramagnetic (FeGe) metal. In the latter case recent experiments have shown that the helical ordering temperature ($T_C = 280$ K at ambient pressure) can be suppressed by the application of external pressure [3]. Furthermore, anomalies in internal structural parameters in cubic FeGe ($\varepsilon$-FeGe) for isothermal compression seem to be related to the magnetic phase boundary line. Here we present single crystal data at ambient conditions as well as in detail the results of the powder diffraction data at high pressure and temperatures as low as 82 K.

2. Sample growth and characterization

Single crystals of $\varepsilon$-FeGe were grown by chemical vapor transport using iodine as transport agent [4] in a homemade two zone furnace. $\varepsilon$-FeGe crystallized very slowly by an endothermal transport reaction from 850 to 810 K although the transport was made perpendicular to the tube axis [5]. The resulting crystals had a volume of less than 1 mm$^3$. Pieces used in the subsequent experiments were examined thoroughly by various X-ray techniques and electron-beam microanalysis.

The wavelength-dispersive-X-ray-analysis (WDX) performed on a microprobe (CAMECA SX100, W-cathode) confirms the ratio Fe:Ge = 1:1 of the crystals and X-ray spectra excited by electron beam (25 keV, 20 nA) showed only lines of both elements. The evaluation of the background intensities at energies of Si-K and I-L-lines allowed us to exclude impurity concentrations larger than 0.08 wt% for both elements involved in the preparation process. Microstructures prepared from crystals by metallographic methods contained small, disoriented areas which show...
unusual strong orientation in the scanning electron microscope images using back-scattered electron (BSE) contrast as well as in polarized light of the light microscope (cf. Fig. 1).

3. Single crystal structure determination

The crystal structure of \( \varepsilon \)-FeGe was solved and refined from single crystal intensity data (Rigaku R-Axis Spider, Ag-K\( \alpha \) radiation, \( \lambda = 56.080 \) pm, rotating anode-microsource, with mirror optic, \( \omega \)-scan, \( \Delta \omega = 1.0^\circ \), 160 images; \( 2\theta_{\text{max}} = 122.6^\circ \), empirical absorption correction). For the structure refinement a full-matrix least squares on \( F^2 \) on eight parameters was performed using SHELXL-97 [6]. A summary of the refinement data is given in Tables 1 and 2. The lattice parameter was determined from powder data [7].

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|---------------------------------------------|
| Density (g cm\(^{-3}\)) | 8.22 |
| \( \mu \) (cm\(^{-1}\)) | 219 |
| Measured and unique reflections | 3680; 1025 |
| Obs. reflections > 4.0 \( \sigma(Fo) \) | 1001 |
| \( R_{\text{int}} \) | 0.018 |
| \( R1; wR2 \) | 0.020; 0.026 |
| Goof = S | 1.209 |
| Flack parameter | 0.0023(105) |
| \( \Delta P_{\text{max}}; \Delta P_{\text{min}} \) (e10\(^6\) pm\(^3\)) | 2.05; −1.01 |

A summary of the refinement data is given in Tables 1 and 2. The lattice parameter was determined from powder data on 12 reflections with the program package CSD [7] (image plate Guinier camera HUBER G670, Co-K\( \alpha \) radiation, \( \lambda = 178.8965 \) pm, LaB\(_6\) (\( \alpha = 415.692 \) pm) as internal standard, \( T = 295 \) K). All structural parameters are given in Table 3.

In the \( B20 \) structure (space group \( P2_13 \), No. 198, \( Z = 4 \)) both atoms occupy 4\( a \) (\( x, x, x \)) Wyckoff positions (Fig. 2). In a binary compound MA crystallizing in the ideal \( B20 \) structure (\( x_M = 0.1545 \), \( x_A = 1 - x_M \)) both atoms have a sevenfold coordination which lies between that of the two simplest binary cubic structures of NaCl (CN = 6) and CsCl (CN = 8). \( \varepsilon \)-FeGe, however, attains a distorted rock-salt structure where the atoms are slightly shifted from their ideal position (\( x_{\text{Fe}} = 0.13522(2) \) and \( x_{\text{Ge}} = 0.84186(1) \)). This results in one short Fe–Ge distance, \( d_1 = 238.78 \) pm, along the trigonal axis pertinent to the Fe atom as well as two longer ones, \( d_2 = 244.57 \) pm and \( d_3 = 264.45 \) pm, between the third second and third third-nearest neighbors, respectively (see Fig. 3). Thus, the coordination sphere of Fe is build up of seven Ge atoms describing a strong distorted monocapped trigonal prism.

Fig. 1. Microstructure of well-facettet \( \varepsilon \)-FeGe-sample (scanning electron microscope image, BSE contrast) is dominated by single crystalline area (homogenous gray) and cavity (black) at the center. A small, disoriented area (darker gray) next to the central hole shows weak contrast in the BSE image but no significant differences in composition is found by WDX measurements.

Fig. 2. Projection of the crystal structure of \( \varepsilon \)-FeGe along [1 0 0]. The symbols (Fe: dark spheres, Ge: light spheres) show the position of the \( 2 \) screw axis. The lines indicate the shortest Fe–Ge distance.

Table 1

| Details of the crystal structure analysis of \( \varepsilon \)-FeGe at ambient pressure and \( T = 295 \) K. |
|---------------------------------------------|
| Density (g cm\(^{-3}\)) | 8.22 |
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Table 2

| Anisotropic displacement parameter \( U_{ij} \) (in pm\(^2\)) for \( \varepsilon \)-FeGe |
|-------------------------------------------|
| \( U_{11} = U_{22} = U_{33} \) | \( U_{23} = U_{13} = U_{12} \) |
| Fe | 57(2) | −6(1) |
| Ge | 55(2) | 0(1) |

The \( U_{eq} \) is defined as one third of the orthogonalized \( U_{ij} \) tensor.

Table 3

| Structural parameters of \( \varepsilon \)-FeGe at ambient conditions and for comparison data of \( \varepsilon \)-FeSi taken from Ref. [9]. |
|-------------------------------------------|
| \( \varepsilon \)-FeGe | \( \varepsilon \)-FeSi |
| \( a \) (pm) | 469.95(2) | 449.5(2) |
| \( V_0 \) (10\(^6\) pm\(^3\)) | 103.79(1) | 90.8 |
| \( x_{\text{Fe}} \) | 0.13522(2) | 0.13650(2) |
| \( x_{\text{Ge}} \) | 0.84186(1) | 0.84262(5) |
| \( d_1 \) (pm) | 238.78(2) | 228.8 |
| \( d_2 \) (pm) | 244.57(1) | 234.6 |
| \( d_3 \) (pm) | 264.45(1) | 251.98 |
| \( d_{\text{FeGe}} \) (pm) | 288.11(2) | 275.6 |
| \( d_{\text{FeSi}} \) (pm) | 291.13(2) | 278.3 |

In the standard setting the fractional coordinates are \( x_{\text{Fe}} = 0.38522(2) \), \( x_{\text{Si}} = 0.09186(1) \) for \( \varepsilon \)-FeGe and \( x_{\text{Fe}} = 0.38650(2) \), \( x_{\text{Si}} = 0.09262(5) \) for \( \varepsilon \)-FeSi. \( A \) denotes either Ge or Si.
4. Powder data at high pressure

The structural evolution with pressure at different temperatures was determined by angle-dispersive X-ray diffraction experiments at the beamline ID09 at the European Synchrotron Radiation Facility. The diffraction patterns were collected at a wavelength of $\lambda = 41.254$ pm during a 10 s exposure time with an image plate. For these measurements well ground and annealed powder (at 670 K for two days) was loaded in a diamond-anvil cell. Helium was used as pressure medium and the pressure was determined via the fluorescence peaks of SrB$_4$O$_7$:Sm$^{2+}$ [8].

Fig. 4(a) shows two examples of a full profile structure refinement (program package CSD [7]) of the diffraction pattern recorded at 82 K. The intensities can be very well refined though with little less precision at the highest pressure. Thus, the fractional atomic parameters $x$$_{Fe}$ and $x$$_{Ge}$, and hence the interatomic distances could be deduced.

The refinement of the diffraction pattern measured at 82 and 230 K revealed clear indications that the shortest interatomic Fe–Ge distance, $d_1$, which is parallel to $[1 1 1]$, changes its pressure dependence discontinuously (Figs. 4(b) and 5(a)). The extrapolation of the low-pressure $d_1(p)$ behavior for 82 and 230 K described by an appropriate equation-of-state (EOS) clearly fails to account for the pressure dependence above 15.8 and 12 GPa, respectively. These anomalies in $d_1(p)$ agree remarkably well with the $T_C(p)$-phase boundary deduced from the electrical resistivity measurements reported in Ref. [3]. The two remaining Fe–Ge distances as well as all distances at room temperature (Fig. 5(b)) decrease smoothly with pressure and no anomaly is seen within the error bars.

The $V(p)$ dependencies of $\varepsilon$-FeGe at all investigated temperatures revealed no discontinuous pressure dependence and that the compression is reversible (cf. insets to Figs. 4(b) and 5). All $V(p)$ can be described by a Murnaghan EOS [10]. The resulting fitting parameters are given in Table 4. The bulk modulus of $\varepsilon$-FeGe is considerably smaller than that of $\varepsilon$-FeSi which is ranging from $B_0 = 160(1)$ GPa ($B' = 4.0$) [11] to 209(6) GPa ($B' = 5.3$) [12]. A simple comparison of the unit-cell volume and using the compressibility of $\varepsilon$-FeGe shows that $\varepsilon$-FeGe attains the same unit-cell volume as $\varepsilon$-FeSi at about 25 GPa. Theoretical studies on $\varepsilon$-FeSi predict a phase transformation to the B2 structure (CsCl-type) at about 13 GPa [13] or in the range of 30–40 GPa [14]. On the other hand, no phase transformation in $\varepsilon$-FeSi has been found up...
to 50 GPa [12]. Thus, more structural information at pressures well above 30 GPa is needed to resolve the stability of $\varepsilon$-FeGe.

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Fig. 5. Pressure dependence of the interatomic Fe–Ge distances $d_1$ and $d_2$ (left scale) and $d_3$ (right scale). Error bars represent 3σ. The lines represent a Murnaghan EOS fit to the data. (a) $T = 230$ K data set, where $d_1(p)$ shows a discontinuity at about 12 GPa; (b) $T = 295$ K data set, where no anomaly in $d_1(p)$ is observed. Insets: $V(p)$ data and EOS fit. Data obtained on decreasing pressure are shown as open symbols.

Table 4

Bulk modulus $B_0$, and its pressure derivative $B'$ of $\varepsilon$-FeGe obtained from a fit of the Murnaghan EOS to the $V(p)$ data

| $T$ (K) | $B_0$ (GPa) | $B'$ |
|--------|-------------|------|
| 295    | 130(1)      | 4.7(1) |
| 230    | 133(1)      | 4.7(1) |
| 82     | 147(3)      | 4.4(2) |