FAST TRACK COMMUNICATION

The synthesis, and crystal and magnetic structure of the iron selenide BaFe_2Se_3 with possible superconductivity at $T_c = 11$ K

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Abstract

We report on the synthesis of single crystals of BaFe_2Se_3 and study their crystal and magnetic structures by means of synchrotron single-crystal x-ray and neutron powder diffraction. The crystal structure has orthorhombic symmetry and consists of double chains of FeSe_4 edge connected tetrahedra intercalated with barium. Below 240 K, long range spin-block checkerboard antiferromagnetic order is developed. The magnetic structure is similar to one observed in $\text{A}_{0.8}\text{Fe}_{1.6}\text{Se}_2$ ($\text{A} = \text{K}, \text{Rb}$ or Cs) superconductors. The crystals exhibit a transition to the diamagnetic state with an onset transition temperature of $T_c \sim 11$ K. Though we observe FeSe as an impurity phase ($<0.8\%$ mass fraction) it is not likely that the diamagnetism is attributable to the FeSe superconductor, which has $T_c \approx 8.5$ K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

With the discovery of alkali metal intercalated FeSe superconductor [1] with the transition temperature $T_c \approx 30$ K, a chalcogenide analog to the 122 iron pnictide superconductors [2, 3] was found. Shortly after the first reported synthesis [1] of $\text{K}_{0.8}\text{Fe}_2\text{Se}_2$ (K122), further compounds with the formula $\text{A}_x\text{Fe}_{2-y}\text{Se}_2$ intercalated with $\text{A} = \text{Cs}$ [4], Rb [5], Tl/K [6] and Tl/Rb [7] were successfully prepared. For all of these superconductors, critical temperatures around 30 K were found. All the intercalated chalcogenides, in contrast to the pnictides, can be relatively easily grown as high quality single crystals by the Bridgman method. This is extremely important, as for many

studies, e.g. neutron scattering experiments, cm^3 size single crystals are required. For $\text{Cs}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ and $\text{K}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ it was found that the empirical dependence of T_c on the anion height (the distance between Fe and the chalcogenide/pnictide layers), as stated for pnictides [8], is also fulfilled [4]. Thus, further increasing T_c (the maximum value for pnictides is ~ 55 K) by applying pressure could potentially be possible. Unfortunately, a negative pressure effect with suppression of the superconductivity above 8 GPa for $\text{Cs}_{0.8}\text{Fe}_{2-y}\text{Se}_2$ was observed [9]. Further, for the $\text{A}_x\text{Fe}_{2-y}\text{Se}_2$, coexistence of superconductivity and a strong magnetism ($T_N \approx 478.5$ K) was found [10]. On the basis of neutron scattering experiments, structure models revealing iron vacancies and magnetic orderings were proposed [11–14].

Figure 1. Crystal structure of Ba123 selenide. In this representation, coordination polyhedra for Fe are shown instead of those for Ba. The double chains of FeSe tetrahedra are edge shared and propagated along the *b*-axis.

In our attempt to explore ternary iron chalcogenides we gave attention to alkaline earth metal families. According to Iglesias and Steinfink [15], in the case of the barium transition metal chalcogenides $\text{Ba}_x\text{M}_y\text{X}_z$ (where $\text{M} = 3\text{d}$ metal, $\text{X} = \text{Se}$ or S), compounds with different stoichiometries $x:y:z$ of 2:1:3, 1:1:2, 1:4:3, 1:2:2 and 1:2:3 could be synthesized. For all these compounds, nine different structure types have been found, all of them based on columns of face-sharing BaX_6 triangular prisms (tetrahedra). In BaMX_2 (Ba112) and BaM_2X_2 (Ba122), sheets are created by edge sharing of the neighboring columns, whereas both in BaM_2X_3 (Ba123) and in BaM_4X_3 (Ba143), the columns are isolated [15]. In particular, Ba123 seems to be an interesting analog to K122, as the additional charge of the alkaline earth metal is balanced by the additional chalcogenide anion in the formula. Figure 1 shows the crystal structure model of orthorhombic Ba123, emphasizing the coordination of the Fe atoms. In contrast to the case for alkali metal intercalated chalcogenides (like K122), the Fe–Se layers are here not two dimensional, but consist of double chains of FeSe_4 edge connected tetrahedra.

In this work, BaFe_2Se_3 (Ba123) single crystals were grown for the first time by the Bridgman method. In contrast to the K122 single crystals, the Ba123 ones are stoichiometric, showing no vacancies in either alkaline earth or iron sublattices. Further, the iron–selenium layer in the structure has Fe_2Se_3 stoichiometry and is created from double chains of FeSe_4 edge connected tetrahedra. Ba123 shows long range antiferromagnetic order at temperatures below 250 K and traces of superconductivity, with the onset at $T_c \approx 11$ K.

2. Experimental details

Single crystals of BaFe_2Se_3 were grown from the melt using the Bridgman method. High purity (at least 99.99%, Alfa) powders of iron and selenium were mixed in the appropriate proportions and pressed into rods. For the single-crystal

synthesis, a piece of Fe_2Se_3 rod was sealed in a double-wall evacuated silica ampule with a stoichiometric amount of pure barium. The ampule was annealed at 1150°C for 24 h for homogenization. Afterwards the melt was cooled down to 750°C with a rate of 6°C h^{-1} and kept at this temperature for the next 20 h. Finally the furnace was cooled down to room temperature at the rate 200°C h^{-1} . Well-formed black crystal rods of 7 mm diameter (the inside diameter of the quartz ampule) were obtained. The crystals could be easily cleaved into plates with flat shiny surfaces. The phase purity of the crystals grown was characterized by means of powder x-ray diffraction (XRD) using a D8 Advance Bruker AXS diffractometer with $\text{Cu K}\alpha$ radiation. For these measurements a fraction of the crystal was cleaved, pulverized, and loaded into the low background airtight specimen holder. All the work was performed in a He glove box to protect the powder from oxidation.

The homogeneity and elemental composition of the cleaved crystals were studied using x-ray fluorescence spectroscopy (XRF, Orbis Micro-XRF Analyzer, EDAX). Elemental distribution maps for Ba, Fe and Se were collected in vacuum, applying white x-ray irradiation produced by an Rh tube (35 kV and $500\ \mu\text{A}$). The x-ray primary beam was focused to a spot of $30\ \mu\text{m}$ diameter. A primary-beam Ti filter ($25\ \mu\text{m}$ thickness) was applied. An area of $\sim 0.5\ \text{cm}^2$ was scanned. Prior to the measurements, elemental calibration was carried out using as a standard a carefully weighted, homogenized mixture of Se, Fe and BaCO_3 , pressed into pellets. The calibration procedure applied results in $\sim 1.5\%$ accuracy of the stoichiometric coefficient values determined.

Single-crystal x-ray data for BaFe_2Se_3 were collected on the SNBL beamline BM1A at the ESRF synchrotron in Grenoble (France) with a KUMA6 diffractometer equipped with the TITAN CCD detector, with $\lambda = 0.69736(1)\ \text{\AA}$, using a combination of ω - and φ -scans in 1° steps and a readout pixel resolution of $62\ \mu\text{m}$. The sample was mounted in a cryo-loop and cooled down to 150 K with an Oxford Cryostream 700+ N_2 blower. The distance from the crystal to the detector was calibrated using the lattice dimensions of the powder sample prepared from the crushed crystals. The intensities were integrated using CrysAlis [16]. The empirical absorption correction was made using the SADABS procedure [17]. The structure solution was performed with SHELXS and the structure refinement with SHELXL97 [18]. Powder diffraction data were collected at the MAR345 detector at the same beamline as the single-crystal data (SNBL, ESRF). The crystal-to-detector distance was calibrated with the LaB_6 NIST standard, the data were processed with Fit2D [19] and local software was used to estimate the standard deviations of the measured intensities. Neutron powder diffraction experiments (NPD) were carried out at the SINQ spallation source of the Paul Scherrer Institute (PSI, Switzerland) using the high resolution diffractometer for thermal neutrons, HRPT [20], with a neutron wavelength $\lambda = 1.886\ \text{\AA}$. The sample was loaded into a vanadium container with an indium seal in a He glove box. Refinements of the crystal and magnetic structures from the powder diffraction data were carried out with the FULLPROF

Figure 2. Three slices of the reciprocal space for the Ba123 single crystal obtained by means of synchrotron diffraction at $T = 150$ K.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3 \text{ \AA}^2$) for 150 K. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Ba(1)	1854(1)	2500	5223(1)	16(1)
Se(2)	3569(2)	2500	2308(2)	13(1)
Se(3)	6285(2)	2500	4902(2)	14(1)
Se(4)	4007(2)	2500	8158(2)	16(1)
Fe(5)	4937(2)	7(3)	3526(2)	13(1)

Table 2. Anisotropic displacement parameters ($\times 10^3 \text{ \AA}^2$) for 150 K. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ba(1)	24(1)	6(1)	18(1)	0	3(1)	0
Se(2)	21(1)	4(1)	15(1)	0	-3(1)	0
Se(3)	23(1)	5(1)	13(1)	0	-1(1)	0
Se(4)	23(1)	6(1)	18(1)	0	5(1)	0
Fe(5)	17(1)	8(1)	12(1)	0(1)	0(1)	0(1)

program [21], with the use of its internal tables for scattering lengths and magnetic form factors. The ac magnetization measurements were performed using a quantum design PPMS magnetometer.

3. Results and discussion

Micro-XRF analysis performed on the BaFe_2Se_3 crystals confirmed their homogeneity. The stoichiometric coefficients determined on the basis of micro-XRF mapping were 0.99 ± 0.02 , 1.99 ± 0.04 and 3.00 ± 0.05 for Ba, Fe and Se, respectively.

Figure 2 shows three slices of the reciprocal space for Ba123 single crystal obtained by means of synchrotron diffraction. One can see a pronounced broadening of the reflections that agrees with a needle-like shape of the highly fragile crystals. Such a broadening is also seen in the reciprocal maps normal to the a^* direction, while the $h0l$ section shows much narrower profiles. This observation is consistent with the morphology of the single crystals, which are assembled from numerous blocks misaligned by a rotation, presumably around the longest a -axis. We have also noted a weak rod-like diffuse scattering propagating along a^* that could be tentatively attributed to the stacking faults normal to the a direction. For many crystals tested, the diffraction data can be successfully indexed assuming a few twin components rotated by a few degrees relative to each other. The crystal morphology, mosaicity and diffuse signal agree with a quasi-1D character of the crystal structure, that is built from covalently bound double chains of FeSe_4 tetrahedra weakly packed together with Ba ions.

The results of the single-crystal structural refinement of BaFe_2Se_3 are summarized in tables 1 and 2. The structural model proposed from the single-crystal experiment fitted well to the powder x-ray and neutron diffraction data (figure 2). Notably, there is one very weak additional reflection at $d \approx 5.52 \text{ \AA}$ at $T = 300 \text{ K}$ seen only in the x-ray powder diffraction pattern that is not modeled with the structure of BaFe_2Se_3 ($Pnma$ space group). This peak can be tentatively assigned to $\text{FeSe}_{1.974}$ with the lattice constants $a = 3.7738$, $c = 5.5235 \text{ \AA}$ [21]. Refinement of this impurity phase with the structure model from [22] gives a 0.8% mass fraction. At odds with the powder data case, a summation of the observed frames in the single-crystal experiment does not reveal an additional reflection at about $5.52 \text{ \AA}$; such a procedure implies an averaging of the single-crystal data set over all orientations of the same crystal and is similar to the powder averaging over many crystals.

On cooling below $T = 240 \text{ K}$, a set of additional Bragg peaks is observed in the NPD patterns that can be indexed with the propagation vector $k = [1/2, 1/2, 1/2]$. The $Pnma$ space group with $k = [1/2, 1/2, 1/2]$ has two two-dimensional irreducible representations (irreps) that both enter the reducible magnetic representation for the Fe spin sitting in the general (8d) position six times. We have sorted all possible symmetry adapted solutions, with the restriction that the Fe spins have the same magnitude and are oriented either parallel or antiparallel to each other and directed along the crystal axes. There are two solutions for both τ_1 and τ_2 irreps that fit the experimental NPD pattern, as shown in figure 3, excellently, with only one refinable parameter—the moment value. The fit reliability

Table 3. Crystal and magnetic structure parameters of BaFe_2Se_3 refined from NPD at 2 K in the $Pnma$ space group. The isotropic atomic displacement parameter B is in $\text{\AA}^2$. χ^2 is the global chi-square values (Bragg contribution), R_B is a reliability Bragg factor, given for the nuclear and magnetic phases separately, and m is the magnetic moment amplitude in μ_B —all are given for two magnetic models (τ_1 , τ_2).

a ($\text{\AA}$)	11.890 33(14)				
b ($\text{\AA}$)	5.407 98(5)				
c ($\text{\AA}$)	9.137 52(11)				
	x	y	z	B	Mult.
Ba1	0.185 14(30)	1/4	0.522 08(51)	0.442(72)	4
Fe1	0.494 04(15)	0.001 48(38)	0.352 63(18)	0.695(25)	8
Se1	0.355 03(25)	1/4	0.232 84(32)	0.777(56)	4
Se2	0.630 36(21)	1/4	0.490 47(31)	0.434(50)	4
Se3	0.401 49(23)	1/4	0.817 31(29)	0.398(47)	4
	$m \parallel a \text{ Fe1}$		χ^2	$R_{B(\text{nucl})}$	$R_{B(\text{magn})}$
τ_1	2.101 (13)		3.82	3.04	4.76
τ_2	2.101 (13)		3.82	3.03	4.84

Figure 3. (a) The NPD pattern, the calculated profile and the difference plot for BaFe_2Se_3 at 2 K. The rows of ticks show the Bragg peak positions for the nuclear and magnetic phases. The magnetic contribution together with the background is shown by the red line. (b) A fragment of the diffraction pattern at low 2θ showing the magnetic contribution.

R -factors for these two models are the same in the refinements of the powder diffraction data. All other magnetic models give significantly poorer R -factors (30–60%). The Fe spins

Figure 4. Refined magnetic structure models ((a) and (b)) for Ba_{123} . The magnetic structures for τ_1 (a) and τ_2 (b) are shown in the projection on the bc -plane. The black and red circles correspond to the up and down spin directions. The Se_2Fe_3 double chains separated by a distance of approximately $a/2$ along the a -axis are shown with a different background color.

have moment $2.1 \mu_B$ and are directed along the a -axis, i.e. perpendicular to the Fe_3Se_2 double chains. The projection of the magnetic structure on the bc -plane is shown in figure 4. It is interesting that the magnetic configuration τ_1 with the four spins forming a ferromagnetic block is similar to the spin-block checkerboard structure observed in $\text{A}_{0.8}\text{Fe}_{1.6}\text{Se}_2$ ($A = \text{K, Rb or Cs}$) [11–14]. A description of the structure model and the magnetic and structure parameters and the details of the refinements at 2 K are summarized in table 3.

Figure 5 shows the temperature dependence of the magnetic moment on Fe. It is evident that the long range antiferromagnetic (AFM) order disappears quite abruptly above 240 K. However the short range AFM correlations persist up to room temperature. At 240 K the magnetic peak width starts to increase and at 250 K and higher, the peak width is about ten times larger than that at low temperature (see figure 5(b)). The domain size estimated from

Figure 5. (a) Temperature dependence of the magnetic moment on Fe. Above $T_N = 240$ K the long range AFM order is destroyed, and the moments in this region correspond to the fit of the broad Lorentzian peak centered approximately at the zero satellite ($1/2, 1/2, 1/2$) at $2\Theta \approx 12^\circ$, assuming the same magnetic model; (b) NPD patterns taken at $T = 230$ and 250 K. Note the change of the magnetic peak width at $2\Theta \approx 12^\circ$.

Figure 6. Temperature dependence of the real part of the ac magnetic susceptibility for BaFe_2Se_3 (black squares) together with $\text{FeSe}_{0.98}$ (red circles).

the AFM Bragg peak broadening amounted to >650 Å at low temperature and about 20 Å at room temperature.

Figure 6 presents the temperature dependence of the real part of the ac magnetic susceptibility for a BaFe_2Se_3 sample measured in a magnetic field of 1 Oe and at a frequency 1000 Hz. The sample exhibits a clear transition to the diamagnetic, possibly superconducting state with an onset transition temperature above $T_c \sim 11$ K. However, the possible superconducting volume fraction is only about 1%. For comparison, a typical magnetization curve for $\text{FeSe}_{0.98}$, the only stated impurity phase, is also shown in the same plot. One can clearly see that the onset transition for BaFe_2Se_3 is at least 2.5 K higher than those for $\text{FeSe}_{0.98}$ (8.33(11) [22], 8.21(4) [23]). Therefore, the diamagnetism above 8.5 K cannot be attributed to the presence of an FeSe impurity phase.

4. Summary

Successful crystal growth of the alkaline earth intercalated iron selenide BaFe_2Se_3 (Ba123) is reported. The crystal structure is similar to that of the analog alkali metal intercalated chalcogenides, with the difference being the one-dimensional arrangement of the FeSe_4 edge connected tetrahedra creating double chains running along the b -axis within the Fe_2Se_3 bc -layers. AFM long range order is observed below $T_N \approx 240$ K. The AFM structure contains four-spin ferromagnetic blocks oriented antiparallel along the Fe_2Se_3 chains with Fe moments of $2.1 \mu_B$ along the a -axis. Short range AFM order is preserved at least up to room temperature. The diamagnetic transition with an onset at about 11 K suggests the possible existence of a superconducting state.

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