A catastrophic charge density wave in $BaFe_2Al_9$

Supplemental Information

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Abstract

Neutron powder diffraction refinement

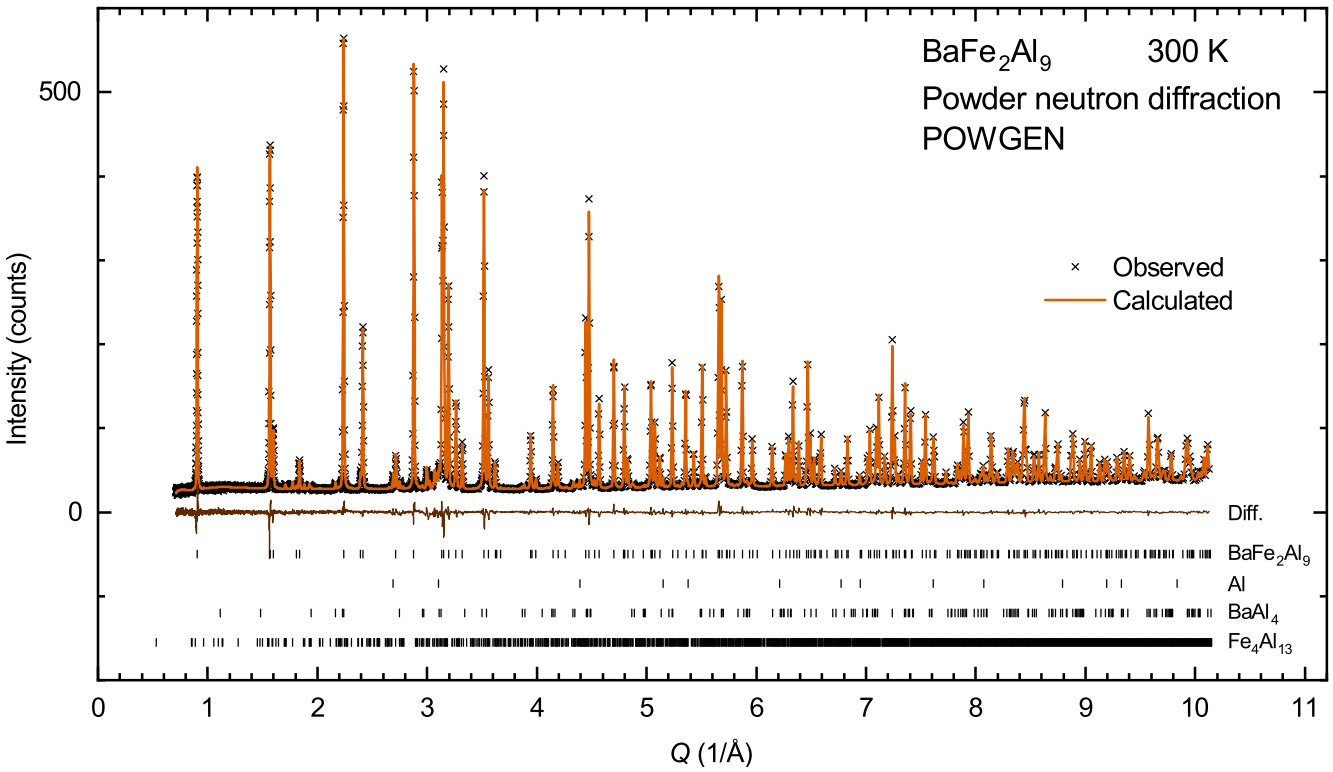

Figure 1: Fit of the 300 K neutron powder diffraction data taken at POWGEN.

Figure 1 depicts the fit to the powder neutron diffraction of $BaFe_2Al_9$ taken at 300 K. We were not selective with the crystals chosen to grind into the 1.83 g sample. As a result, this measurement represents a worst-case scenario for impurities. The refinement indicates 92.2(3) wt% $BaFe_2Al_9$, 1.14(7) wt% Al metal, 2.62(19) wt% $BaAl_4$, and 4.00(12) wt% Fe_4Al_{13}.

Tables 1 presents the details of the structure refinement from the powder neutron diffraction data of $BaFe_2Al_9$ above and below the charge density wave (CDW) transition. Although the compound has a CDW modulation at 50 and 7 K the same structure model was used for all temperatures. This was done because no super-lattice peaks are observed in the neutron data to refine a modulated structure. We were able to infer the presence of a CDW modulation in the average structure based on the atomic parameters in Tables 2 and 3. As discussed in the main text, the anisotropic atomic displacement parameters (ADPs) show an anomalous temperature dependence below 100 K consistent with the CDW model we

propose.

Our refinement indicated that the Fe site in $BaFe_2Al_9$ mostly occupied with only a few percent vacancies. This reduced site occupancy was also observed when x-ray data were refined.

Table 1: Neutron powder refinement details from POWGEN time of flight data.

Chemical formula	$BaFe_{1.92}Al_9$			
Formula wt. (g/molF.U.)	487.383			
Crystal system	hexagonal			
Space group	$P6/mmm$ (191)			
Temperature (K)	300	120	50	7
a (Å)	8.018667(16)	8.006172(15)	8.04357(3)	8.04363(3)
c (Å)	3.934816(14)	3.929166(13)	3.86933(3)	3.86835(3)
V (Å^3)	219.1086(10)	218.1127(9)	216.8024(19)	216.7509(18)
Z	1			
Density calculated (g/cm^3)	3.7277	3.7447	3.7674	3.7683
wavelength range (Å)	0.97 - 2.033			
F(000)	494.718	494.718	482.026	494.718
Time of flight range (ms)	11.3 - 315			
No. of variables	46			
RF(obs)	1.15	1.17	2.7	2.65
RFw(obs)	1.58	1.69	4.4	4.15
Goodness of fit	2.8	3	4.58	4.27
Absorption	0.077(2)	0.077(2)	0.078(4)	0.074(3)

Mössbauer fits

In the results section we note an inconsistency between out Mössbauer spectra from $BaFe_2Al_9$ and the charge density wave modulation presented in Fig. 3d. Specifically, the observed super-lattice reflections from single crystal x-ray diffraction signal a simple sine-modulation of the atomic positions. This should give a distribution of Fe atom environments with a range of Mössbauer parameters. For example, a sine-modulation of the quadrupole parameter would yield the orange distribution of values in the left panel of Fig. 2. This contrasts with the discrete pair of values from a fit to the two Fe-site model (thick black line).

Table 2: Neutron refinement $BaFe_2Al_9$ atomic parameters

Atom	Site	x	y	z	$U_{aniso.}$	Occupancy
			300 K			
Al1	$3f$	$\frac{1}{2}$	0	0	0.0099(2)	1
Al2	$6m$	0.21481(4)	0.42961(8)	$\frac{1}{2}$	0.0089(2)	1
Ba	$1a$	0	0	0	0.0126(3)	1
Fe	$2c$	$\frac{1}{3}$	$\frac{2}{3}$	0	0.0067(1)	0.984(3)
			120 K			
Al1	$3f$	$\frac{1}{2}$	0	0	0.0059(2)	1
Al2	$6m$	0.21484(4)	0.42968(8)	$\frac{1}{2}$	0.0055(2)	1
Ba	$1a$	0	0	0	0.0064(2)	1
Fe	$2c$	$\frac{1}{3}$	$\frac{2}{3}$	0	0.0045(1)	0.985(3)
			50 K			
Al1	$3f$	$\frac{1}{2}$	0	0	0.0055(4)	1
Al2	$6m$	0.21355(7)	0.42711(13)	$\frac{1}{2}$	0.0077(3)	1
Ba	$1a$	0	0	0	0.0101(4)	1
Fe	$2c$	$\frac{1}{3}$	$\frac{2}{3}$	0	0.0127(2)	0.988(5)
			7 K			
Al1	$3f$	$\frac{1}{2}$	0	0	0.0053(3)	1
Al2	$6m$	0.21354(6)	0.42707(12)	$\frac{1}{2}$	0.0076(3)	1
Ba	$1a$	0	0	0	0.0093(4)	1
Fe	$2c$	$\frac{1}{3}$	$\frac{2}{3}$	0	0.0125(2)	0.985(5)

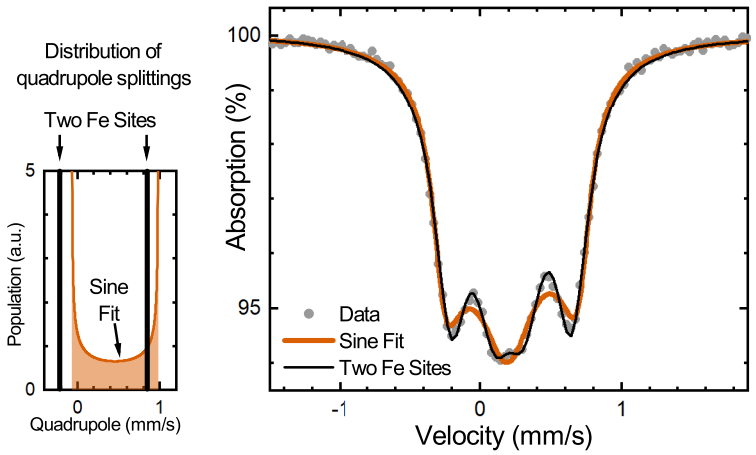

Figure 2: Fits of [54] Mössbauer spectra from $BaFe_2Al_9$ in the charge density wave phase at 15 K. The left panel shows the distribution of quadrupole parameters for two Fe sites model (black) and the sine-modulated quadrupole model that best fit the spectra. The right hand plot shows that two-site model (black) fits the measured spectra (gray points) better than the sine modulated model (orange).

Table 3: Neutron refinement $BaFe_2Al_9$ atomic displacement parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}
		300 K		
Al1	0.0128(3)	0.0071(4)	0.0078(4)	0.00356(18)
Al2	0.0093(2)	0.0105(2)	0.0073(3)	0.00525(12)
Ba	0.0156(3)	0.0156(3)	0.0067(5)	0.00782(17)
Fe	0.00598(15)	0.00598(15)	0.00898(19)	0.00299(7)
		120 K		
Al1	0.0073(3)	0.0056(3)	0.0043(3)	0.00282(17)
Al2	0.00589(19)	0.0069(2)	0.0040(3)	0.00344(11)
Ba	0.0083(3)	0.0083(3)	0.0026(4)	0.00414(14)
Fe	0.00389(14)	0.00389(14)	0.00570(17)	0.00195(7)
		50 K		
Al1	0.0049(4)	0.0045(5)	0.0069(6)	0.0022(3)
Al2	0.0064(3)	0.0107(4)	0.0073(5)	0.0054(2)
Ba	0.0125(5)	0.0125(5)	0.0052(7)	0.0063(2)
Fe	0.0038(3)	0.0038(3)	0.0305(4)	0.00188(13)
		7 K		
Al1	0.0048(4)	0.0046(5)	0.0064(5)	0.0023(2)
Al2	0.0064(3)	0.0108(4)	0.0070(4)	0.00539(19)
Ba	0.0118(4)	0.0118(4)	0.0044(7)	0.0059(2)
Fe	0.0035(2)	0.0035(2)	0.0305(4)	0.00176(12)

We tried to fit the low temperature Mössbauer spectra of $BaFe_2Al_9$ with such a modulated model. We summed the spectra of 20 sites with sine-modulated Mössbauer parameters. The maximum and minimum values of the quadrupole splitting, isomer shift and linewidth were allowed to vary and the best fit is given by the orange curve on the right-hand plot of Fig. 2. This fit is distinctly worse than the two iron site model in black presented in the main text.