Preparation, characterization and DFT+*U* study of the polar Fe^{3+}-based phase $Ba_5Fe_2ZnIn_4S_{15}$ containing S= 5/2 zigzag chains

Batoul Almoussawi[a], Victor Duffort[a], Angel M. Arevalo-Lopez[a], Maxime Braun[a], Nora Djelal[a], Houria Kabbour[a*]

[a] Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

Table S1: Transformation matrices to apply to the atomic coordinates published in references 5 and 6 for direct comparison with the structure reported in the present article.

Composition	Reference	Rotation matrix	Translation vector
$Pb_5ZnGa_6S_{15}$	6	(a, b, c)	(½, 0, 0)
$Sr_5ZnGa_6S_{15}$	5	(a, -b, -c)	(½, 0, 0)

Table S2. Atomic positions found after the full relaxation of the **reported** structure of $Pb_5Ga_6ZnS_{15}$, the optimized parameters are a= 22.1357 Å. b= 17.9791 Å. c= 6.2361 Å.

atom	x/a	y/b	z/c	Wyckoff
Pb1	0.88795	0.63567	0.96695	8c
Pb2	0.89092	0.85321	0.57628	8c
Pb3	0.75	0.35005	0.62541	4b
Ga1	0.75	0.69539	0.59209	4b
Ga2	0.33820	0.96656	0.95109	8c
Ga3	0.75	0.53212	0.92919	4b
Ga4	0.47182	0.6954	0.57029	8c
Zn1	0	0	0	4a
S1	0.75	0.15820	0.45145	4b
S2	0.84330	0.65872	0.47120	8c
S3	0.91798	0.99437	0.75668	8c
S4	0.49052	0.80902	0.72450	8c
S5	0.99948	0.40442	0.75505	8c
S6	0.75	0.82051	0.56244	4b
S7	0.87105	0.79520	0.99046	8c
S8	0.83281	0.47750	0.77946	8c
S9	0.75	0.99008	0.78207	4b

Table S3. Atomic positions found after the full relaxation of the **modified** structure of $Pb_5Ga_6ZnS_{15}$, the optimized parameters are a=22.1740 Å, b=17.9492 Å c=6.2357 Å. The modified sites are highlighted in bold (compared to the reported structure).

atom	x/a	y/b	z/c	Wyckoff
Pb1	0.88000	0.63931	0.97872	8c
Pb2	0.88666	0.85083	0.57157	8c
Pb3	0.75	0.35766	0.62497	4b
Ga1	0.75	0.69607	0.59500	4b
Ga2	0.33762	0.96815	0.96881	8c
Zn1	**0.75**	**0.5321**	**0.9395**	**4b**
Ga4	0.47273	0.69506	0.55657	8c
Ga3	**0**	**0**	**0**	**4a**
S1	0.75	0.16211	0.45239	4b
S2	0.84326	0.65863	0.47155	8c
S3	0.91862	0.99404	0.76467	8c
S4	0.49157	0.80870	0.70955	8c
S5	0.99690	0.59539	0.74418	8c
S6	0.75	0.82161	0.56423	4b
S7	0.87131	0.79775	0.99271	8c
S8	0.83496	0.47714	0.79364	8c
S9	0.75	0.99109	0.79834	4b

Table S4. Atomic positions found after the full relaxation of the **reported** structure of $Sr_5Ga_6ZnS_{15}$, the optimized parameters are a=22.3343 Å, b=18.1860 Å, c=6.1778 Å.

atom	x/a	y/b	z/c	Wyckoff
Sr1	0.25	0.64971	0.42804	4b
Sr2	0.11270	0.15063	0.46323	8c
Sr3	0.11158	0.36484	0.01386	8c
Zn1	0	0	0	4a
Ga1	0.52824	0.30656	0.43757	8c
Ga2	0.65872	0.03480	0.03446	8c
Ga3	0.25	0.46788	0.05469	4b
Ga4	0.25	0.30399	0.39554	4b
S1	0.08298	0.00316	0.23893	8c
S2	0.00163	0.59528	0.24524	8c
S3	0.50524	0.19414	0.28632	8c
S4	0.62950	0.29880	0.48114	8c
S5	0.15682	0.34045	0.51225	8c
S6	0.16667	0.51853	0.20147	8c
S7	0.25	0.34310	0.03209	4b
S8	0.25	0.18051	0.43447	4b
S9	0.25	0.00573	0.19518	4b

Table S5. Atomic positions found after the full relaxation of the **modified** structure of $Sr_5Ga_6ZnS_{15}$. the optimized parameters are a=22.3982 Å. b=18.1004 Å. c=6.1893 Å. The modified sites are highlighted in bold (compared to the reported structure).

atom	x/a	y/b	z/c	Wyckoff
Sr1	0,25	0,65080	0,42792	4b
Sr2	0,11585	0,15208	0,47010	8c
Sr3	0,11749	0,36519	0,01034	8c
Ga3	**0**	**0**	**0**	**4a**
Ga1	0,52784	0,30591	0,45373	8c
Ga2	0,66077	0,03299	0,01964	8c
Zn1	**0,25**	**0,4668**	**0,0474**	**4b**
Ga4	0,25	0,30383	0,39085	4b
S1	0,08187	0,00404	0,22934	8c
S2	0,00200	0,40425	0,25660	8c
S3	0,50441	0,19299	0,30433	8c
S4	0,62822	0,30034	0,48461	8c
S5	0,15709	0,34095	0,51499	8c
S6	0,16394	0,51725	0,18840	8c
S7	0,25	0,33708	0,03150	4b
S8	0,25	0,17979	0,43984	4b
S9	0,25	0,00734	0,18414	4b

Table S6: Atomic coordinates of the hypothetical aristotype of $Ba_5ZnFe_2In_4ZnS_{15}$ in the Amam space group, cell parameters remain unchanged a = 23.458 Å, b = 18.551 Å and c = 6.464 Å.

Atom	Wyck.	x	y	z
Ba1	4c	¾	⅓	½
Ba2	8f	⅝	⅙	½
Ba3	8f	⅛	⅙	½
In1	4a	0	0	0
In2	4c	¾	⅔	½
In3	8f	⅝	½	½
Fe1	8f	½	⅔	½
Zn1	4c	¾	½	0
S1	4c	¾	⅚	½
S2	8f	⅜	⅔	½
S3	16h	½	⅔	¾
S4	4c	¾	⅔	0
S5	8f	⅝	⅔	½
S6	16h	⅝	½	¼
S7	4c	¾	½	½

Table S7: Mode decomposition of $Ba_5ZnFe_2In_4S_{15}$ using the aristotype as parent structure

Mode #	Atom	dx	dy	dz	Amplitude (Å)	Irrep.
1	Ba1	0	0.0381	0	0.3168	
2	Ba2	0	0.027	0	-1.2372	
3	Ba2	-0.0213	0	0	0.4893	
4	Ba3	0	0.027	0	-0.2359	
5	Ba3	-0.0213	0	0	0.7098	
6	In2	0	0.0381	0	0.7557	
7	In3	0	0.027	0	1.1053	
8	In3	-0.0213	0	0	-1.6496	
9	Fe1	0	0.027	0	1.0958	
10	Fe1	-0.0213	0	0	1.3601	
11	Zn1	0	0.0381	0	0.7440	
12	S1	0	0.0381	0	-0.2309	Γ_{1+}
13	S2	0	0.027	0	1.1043	
14	S2	-0.0213	0	0	-0.0624	*Amam*
15	S4	0	0	0.0547	0.0823	
	S3	0	0	-0.0547		Global
16	S4	0	0.0191	0	-0.7792	amplitude
	S3	0	0.0191	0		3.91 Å
17	S4	-0.0151	0	0	-0.3434	
	S3	-0.0151	0	0		
18	S5	0	0.0381	0	-0.2414	
19	S6	0	0.027	0	-0.2548	
20	S6	-0.0213	0	0	-1.3685	
21	S8	0	0	0.0547	-0.4479	
	S7	0	0	-0.0547		
22	S8	0	0.0191	0	-0.7372	
	S7	0	0.0191	0		
23	S8	-0.0151	0	0	0.0418	
	S7	-0.0151	0	0		
24	S9	0	0.0381	0	-0.1653	
25	Ba1	0	0	0.1094	0.6308	
26	Ba2	0	0	0.0774	-0.1293	
27	Ba3	0	0	0.0774	0.3103	
28	In1	0	0	0.1094	0	
29	In2	0	0	0.1094	0.9599	
30	In3	0	0	0.0774	-0.2973	
31	Fe1	0	0	0.0774	0.6723	
32	Zn1	0	0	0.1094	-0.4297	
33	S1	0	0	0.1094	0.5851	Γ_{3-}
34	S2	0	0	0.0774	0.1293	
35	S4	0	0	0.0547	-0.1737	
	S3	0	0	0.0547		*Ama2*
36	S4	0	0.0191	0	-2.6576	
	S3	0	-0.0191	0		Global
37	S4	-0.0151	0	0	0.3659	amplitude
	S3	0.0151	0	0		6.07 Å
38	S5	0	0	0.1094	-0.2468	
39	S6	0	0	0.0774	-0.1551	
40	S8	0	0	0.0547	0.7039	
	S7	0	0	0.0547		
41	S8	0	0.0191	0	0.3804	
	S7	0	-0.0191	0		
42	S8	-0.0151	0	0	2.8285	
	S7	0.0151	0	0		
43	S9	0	0	0.1094	-1.7460	

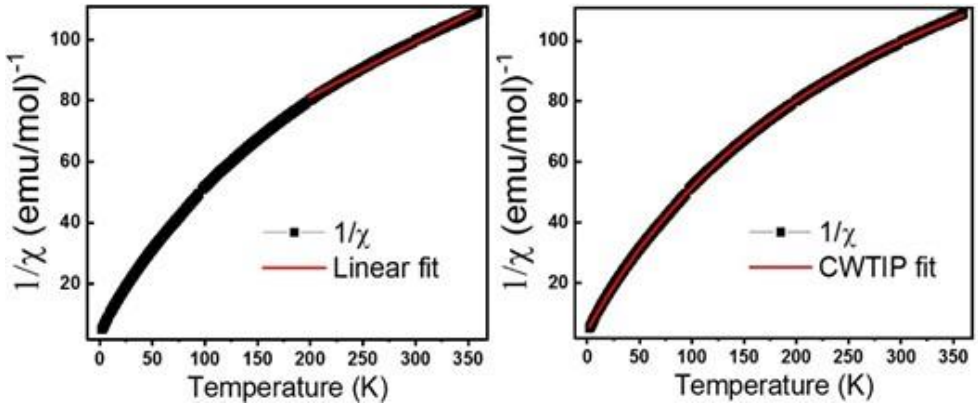

Figure S1. On the right: Linear fit of the reciprocal magnetic susceptibility 1/χ between 200-350K. On the left: CW TIP fit of the reciprocal magnetic susceptibility 1/χ.

Despite the unidentified impurity, we attempted to fit the magnetic data. We have applied a Curie-Weiss fit from 200-350 K, which led to θ_{cw} = -358.08 K and an effective moment of μ_{eff} = 6.689 μ_B per formula unit, based on $Ba_5Fe_2ZnIn_4S_{15}$. It indicates dominating and strong antiferromagnetic interaction which agrees with the DFT calculated exchange interactions described below. However, regarding the presence of Fe^{3+} in a high spin state, the expected theoretical effective moment is of 5.92 μ_B. Our fitted value is far below considering two Fe^{3+} per formula unit. As an alternative and accordingly with the suspicion of a temperature independent paramagnetic (TIP) contribution more visible at high temperature, we applied a Curie-Weiss fit including a TIP contribution. We used the following equation:

$$x = \frac{c}{(T-\theta)} + \alpha$$

where C is the Curie constant, θ is the Curie-Weiss temperature and α is the TIP contribution. It leads to the following parameters with C= 1.540(2) emu.Oe^{-1}.g^{-1}, θ = -7.03(5) K and α= 0.00502(1) emu.Oe^{-1}.g^{-1}. The later TIP contribution is rather high. The extracted effective moment is found about 3.5 μ_B per formula unit, which is even lower than in the standard CW fit. In conclusion, although these preliminary magnetic measurements confirm the dominant antiferromagnetic interactions and point toward a phenomenon around 3 K, it is difficult to extract more information due to the current amount of impurity.

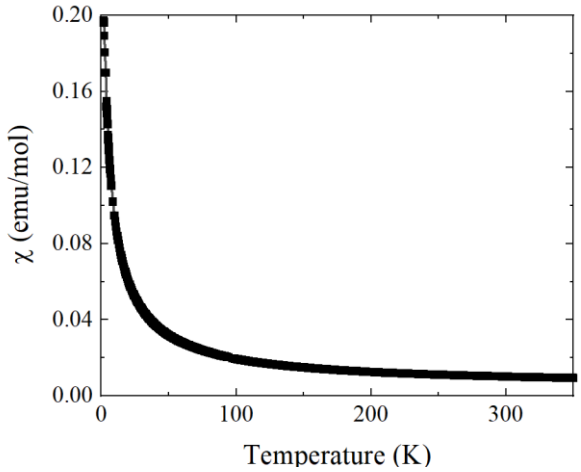

Figure S2. Magnetic susceptibility as a function of temperature in the whole measured temperature range.