The series “Missing chapters of Narjes’ THESIS”: Symmetries of vibration modes in chalcopyrite and kesterite

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We can use the tools of the Bilbao crystallographic server in order to identify Raman and IR-active modes.

Basic structure information:

Chalcopyrite: space group $I\bar{4}2d$ (Nr 122);

atom positions consistent with our setting are

Elem.	Wychoff pos.	Coordinates $(0\ 0\ 0) + (\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$
Cu	a	$(0\ 0\ 0)$, $(\frac{1}{2}\ 0\ \frac{3}{4})$
In	b	$(0\ 0\ \frac{1}{2})$, $(\frac{1}{2}\ 0\ \frac{1}{4})$
Se	d	$(x\ \frac{1}{4}\ \frac{1}{8})$, $(-x\ \frac{3}{4}\ \frac{1}{8})$, $(\frac{1}{4}\ -x\ \frac{7}{8})$, $(\frac{3}{4}\ x\ \frac{7}{8})$ with “perfect” $x = \frac{1}{4}$

(in fact, $x \approx 0.23$)

Kesterite: space group $I\bar{4}$ (Nr 82);
atom positions according to our setting as in the calculations
(alternative settings are possible)

Elem.	Wychoff pos.	Coordinates $(0\ 0\ 0) + (\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$
Cu	a	$(0\ 0\ 0)$
Cu	c	$(0\ \frac{1}{2}\ \frac{1}{4})$
Sn	b	$(0\ 0\ \frac{1}{2})$
Zn	d	$(0\ \frac{1}{2}\ \frac{3}{4})$
Se	g	(x,y,z) $(-x,-y,z)$ $(y,-x,-z)$ $(-y,x,-z)$ with “perfect” (x,y,z)=$(\frac{1}{4}\ \frac{3}{4}\ \frac{1}{8})$

Stannite: space group $I\bar{4}2m$ (Nr 121)

How to proceed:

Go to Bilbao server
`http://www.cryst.ehu.es/`
→ [Sections: Solid State] → [Solid State Theory Applications: SAM]
or directly to
`http://www.cryst.ehu.es/rep/sam.html`
– choose the space group;
– select the concerned Wyckoff positions;
– select to “Show”
– go to “Mechanical representation”
– click to “Show”.

What we see:

For chalcopyrite, there are five irreducible representations where the vibrations of different Wyckoff positions contribute as follows (see “Mechanical Representation”):

W.pos.	A_1	A_2	B_1	B_2	E	$\sum$
(4a)			1	1	2	$1+1+2{\times}2=6$
(4b)			1	1	2	$1+1+2{\times}2=6$
(8d)	1	2	1	2	3	$1+2+1+2+3{\times}2=12$

This sums up to (8 at.)×3 = 24 modes, as expected.

IR active modes: B_2 and E;
Raman active modes: A_1, B_1, B_2, E.

For kesterite, there are three irreducible representations. Note that the two-dimensional one, E, appears in the table represented by its two partners, E^1 and E^2. Their linear combinations, $E^1{\pm}E^2$, yield cartesian X and Y displacements in the modes. The vibrations of different Wyckoff positions contribute as follows (see “Mechanical Representation”):

W.pos.	A	B	E	$\sum$
(2a)		1	1	$1+1{\times}2=3$
(2b)		1	1	$1+1{\times}2=3$
(2c)		1	1	$1+1{\times}2=3$
(2d)		1	1	$1+1{\times}2=3$
(8g)	3	3	3	$3+3+3{\times}2=12$

This sums up to 24 modes, as for chalcopyrite.

IR active modes: B and E;
Raman active modes: all A, B, E.

The “elementary” displacements within each irreducible representation are yielded by clicking on “Show” in the “Mechanical Representation” table for a given Wyckoff position. For instance, the information for (8g) position is the following. There are three modes in each of A, B, E^1+E^2 and E^1-E^2 irreducible representations, which are numbered in the following table:

Anion	A modes			B modes			(E^1+E^2) modes			(E^1-E^2) modes		
sites	#1	#2	#3	#1	#2	#3	#1	#2	#3	#1	#2	#3
$(\frac{1}{4}\,\frac{3}{4}\,\frac{1}{8})$	Y	$-X$	$-Z$	Y	$-X$	Z	X	Y	Z	–	–	–
$(\frac{3}{4}\,\frac{1}{4}\,\frac{1}{8})$	$-Y$	X	$-Z$	$-Y$	X	Z	X	Y	$-Z$	–	–	–
$(\frac{3}{4}\,\frac{3}{4}\,\frac{7}{8})$	X	Y	Z	$-X$	$-Y$	Z	–	–	–	Y	X	$-Z$
$(\frac{1}{4}\,\frac{1}{4}\,\frac{7}{8})$	$-X$	$-Y$	Z	X	Y	Z	–	–	–	Y	X	Z

For all four cations the "elementary" displacements are the same; these are Z in the B-mode, X in the E^1+E^2-mode and Y in the E^1-E^2-mode. Show them in a table, for clarity:

W.pos.	B modes	(E^1+E^2) modes	(E^1-E^2) modes
(2a)	Z	X	Y
(2b)	Z	X	Y
(2c)	Z	X	Y
(2d)	Z	X	Y

Let us summarize what does all this mean. The true vibration modes can mix as they want all the displacements within the same symmetry block. For instance, the A block may contain nothing else than the three modes of purely anionic nature, which can be however any (orthogonal) combinations of the #1, #2 and #3 'basis' A-modes from the above table. For B modes, however, the Z-displacements of cations can be admixed. There will be, in total, 7 B modes, which can in reality come out as 7 orthogonal linear combinations of three anion-only B-type displacements and four single-cation B displacements. We note e.g. that the prototype Γ-zincblende mode, "all cations against all anions", is split into the B-part (which would allow a symmetric all-anions Z displacement *and* the Z displacement of each cation independently), and into the doubly degenerate (E^1,E^2) part: say, combining (E^1+E^2) #1 with (E^1-E^2) #2 for anions with (E^1+E^2) for each cation, as one "basis function", and (E^1+E^2) #2 and (E^1-E^2) #1 for anions with (E^1-E^2) for each cation, as the other "basis function". We note moreover that of the three Γ=0 acoustic modes (all atoms in phase), one will be found in the B block and two - in two partners of the E block. Projecting them out (e.g., taking the unit cell barycenter as a fixed reference point) will leave $3\times A+6\times B+6\times E\rightarrow$ 21 modes, as expected (8 at.$\times$3$-$3). We note that the separation into two orthogonal partners E^1 and E^2 is arbitrary, therefore all possible linear combinations between them can be taken, as long as this results in a system of orthogonal vibration modes.

We come back to chalcopyrite and outline its corresponding basis of "elementary vibrations", offered by the Bilbao machine. The E-representation comes about with its two partners. For anions we have:

Anion	A_1	A_2		B_1	B_2		E, partner 1			E, partner 2		
sites		#1	#2		#1	#2	#1	#2	#3	#1	#2	#3
$(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{8})$	$-X$	$-Y$	Z	$-X$	$-Y$	Z	–	–	X	Z	Y	–
$(\frac{3}{4}\,\frac{3}{4}\,\frac{1}{8})$	X	Y	Z	X	Y	Z	–	–	X	$-Z$	Y	–
$(\frac{1}{4}\,\frac{3}{4}\,\frac{7}{8})$	Y	$-X$	$-Z$	$-Y$	X	Z	$-Z$	X	–	–	–	Y
$(\frac{3}{4}\,\frac{1}{4}\,\frac{7}{8})$	$-Y$	X	$-Z$	Y	$-X$	Z	Z	X	–	–	–	Y

For cations, A_1 and A_2 modes do not contribute anything, and for the rest we have:

	B_1	B_2	E, pa.1		E, pa.2	
sites			#1	#2	#1	#2
(4a)						
(0 0 0)	$-Z$	Z	X	Y	Y	$-X$
$(\frac{1}{2}\ 0\ \frac{3}{4})$	Z	Z	X	Y	$-Y$	X
(4b)						
$(0\ 0\ \frac{1}{2})$	$-Z$	Z	X	Y	Y	$-X$
$(\frac{1}{2}\ 0\ \frac{1}{4})$	Z	Z	X	Y	$-Y$	X

Again we see that the uniform anion vs. cation vibration (the remnant of the zincblende-Γ) *and* the Γ-acoustic modes are hidden in the B_2 block (Z-polarization) and in the E blocks. In the latter, a proper combination of vibrations (e.g., mode #2 + mode #3 of the partner 1 for anions along with mode #1 in the partner 1 for cations) recover the net Cartesian diplacements. We emphasize that all these modes are both Raman and infrared active.

What we'd like to do next is to identify how are the modes of different symmetry related with (presumable) zone-boundary modes of the zincblende prototype; this will hopefully help us to know how to project out contributions to the mode density from different blocks. In a nutshell, in our projection technique we want to multiply the atoms' vibration eigenvectors by *something*, prior to taking summation over atoms, so as to enhance the collective vibration patterns according to one or another irreducible representation. This *something* must include an exponent $\exp(i\mathbf{q}\mathbf{R}_\alpha)$ with $\mathbf{q}$ such that $\tau \cdot \mathbf{q} = 2\pi n$ for any translation vector τ. Moreover, the *something* must be polarization-dependent.

Secondary phase Cu_2SnSe_3, Cu_2SnS_3: space group Cc (Nr 9):
Only $4a$ Wyckoff position: $[(0,0,0)^+;\ (1/2,1/2,0)^+][(x,y,z);(x,-y,z{+}1/2)]$. There are two irreducible representations, A' and A'', both Raman and IR active, 3 modes in each. Table of "Mechanical representations":

	A' modes			A'' modes		
sites	#1	#2	#3	#1	#2	#3
(x,y,z)	Z	Y	X	$-Z$	Y	$-X$
$(x,-y,z{+}1/2)$	Z	$-Y$	X	Z	Y	X