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Lattice Dynamics of Chalcopyrite Type Compounds. Part I. Vibrational Frequencies

This series of papers is dedicated to Prof. Heinz Dieter Lutz on the occasion of his 65th birthday.

To obtain a sound basis for calculations of the lattice dynamics of chalcopyrite type compounds the literature data for the vibrational frequencies of 14 chalcogenides and 8 pnictides crystallizing in this structure are critically analysed. This is done by introducing frequency ratios of those frequencies which can be derived from zone centre or zone boundary vibrations of the sphalerite lattice presuming similar bonding and normal co-ordinates in all compounds investigated. Based on the reliable spectra vibrational frequencies have been calculated for those compounds which have not yet been investigated or for which the results given in the literature are uncertain.

Keywords: chalcopyrite, vibrational spectra

Introduction

A large number of lattice dynamical calculations on chalcopyrite type compounds is found in the literature, which are not directly comparable as they are done on the basis of different models, i.e. Urey-Bradley-Force-field-model, Keating model, rigid-ion-model, and different sets of short range force constants. For a better understanding of the lattice dynamics of this group of compounds we started calculations with a short range model and a rigid ion model for a large group of chalcopyrites, both chalcogenides and pnictides.

Factor group analysis for the zone centre of the chalcopyrite type (SG $I\bar{4}2d - D_{2d}^{12}$, $z=2$) results in following irreducible representation (without the translational degrees of freedom which belong to B_2 and E): $\Gamma = A_1(\text{Ra}) + 3B_1(\text{Ra}) + 3B_2(\text{IR,Ra}) + 6E(\text{IR,Ra})$

As the vibrational spectra found in the literature for chalcopyrite type compounds, which form the basis for the calculations, often are contradictory with respect to wavenumbers and assignment and do not show all 13 vibrational modes predicted by group theory in some cases we started with a critical evaluation and a thorough analysis of the data found in the literature.

Vibrational spectra

The critical analysis of the vibration spectra is based on the postulate of an extensive similarity of structure and bonding - and this includes the normal co-ordinates of the vibrational modes - in the various compounds crystallizing in the chalcopyrite structure. This postulate is founded on the conformity of the patterns found for the IR and Raman-spectra of chalcopyrite type compounds.

The vibrational wavenumbers and their assignment found in the literature are compiled in tables I-V. As can be seen from these tables there are major differences between the experimental results of different authors in some cases. In the short-waved part of the spectrum this may be due to difficulties in the single crystal measurements because of the quality of the crystals (they could be twins or even mosaic crystals) or badly oriented crystal faces, resulting in leakage for instance of modes of species E to a spectrum of species B₂. In the long waved part, which shows weak bands only, impurities and lattice defects can disturb the spectra and complicate the interpretation.

One of the modes which have been determined in nearly all experiments without doubt is the vibration of species A₁ which produces the most intense line in the Raman spectrum. As can be seen from the tables, the vibrational frequencies of this mode are nearly identical for compounds with the same anion and even those for the pnictides and chalcogenides with anions of similar mass are comparable showing that the postulate of similar bonding in the different chalcopyrites is valid.

The A₁-mode was used by MATSUSHITA to look for a correlation of the frequencies with the masses of the cations. But as this mode is a vibration of the anions only, the cations do not move and so not the masses of the cations but the force constants are responsible for the trends in the frequencies of the A₁ mode. Nevertheless, as the cations with higher masses are normally also bigger and due to the larger distances to the anions exhibit lower force constants there is a shift of the A₁ mode to lower frequencies with increasing cation mass. The frequency of the A₁ mode can therefore serve as a probe for a mean value of the force constants in the different chalcopyrite type compounds. This can be seen in the series of compounds CuBS₂ for B=Al, Ga, In where the A₁ vibration shifts from 315 via 312 to 294cm⁻¹ and in CdBP₂ for B=Si, Ge, Sn from 326 via 321 to 301 cm⁻¹; equally decreases the frequency with the mass of the A-cation, for instance in AGaS₂ for A=Cu, Ag from 312 to 295cm⁻¹ and in AGEp₂ for A=Zn, Cd from 328 to 321cm⁻¹ pointing to a decrease of the force constants in the same direction. Furthermore it is observed that the frequencies of the A₁ modes decrease more than is expected from the increase of mass when changing the anion also showing the effect of the lower force constants. So the frequencies of the A₁-modes of CdGeP₂ and CdGeAs₂ are 328 and 196 cm⁻¹, respectively, while one would expect a value of 205cm⁻¹ for CdGeAs₂ according to the mass change of the anion only. A comparison of the two groups of chalcopyrites, the chalcogenides and the pnictides, shows that the pnictides exhibit higher frequencies by about 5 – 10% in all cases when compared with a chalcogenide of similar mass.

The most intense bands in the IR-spectra of the chalcopyrites are normally those of the B₂¹-, B₂²-, E¹- and E³-modes. Of these the B₂¹- and E¹-vibrations are called sphalerite-modes as they can be derived from the Γ₁₅-vibration of the sphalerite lattice according to BAHR. Looking to these frequencies more closely one notices in all chalcopyrites ABX₂ with the same B-cation a slight variation of these values only. Obviously the A-cation does not move during these vibrations. Accordingly one obtains linear correlations when plotting 1/μ(B) vs. ω² (see BAHR). This applies in nearly the same way to the modes B₂²- and E³, whose frequencies correlate with the reduced mass of the A-cation.

The inference of the modes of species E, B₁ and B₂ from the vibrations of the sphalerite-lattice and the observation that there is a slight deviation from cubic symmetry only lead to the assumption that the frequencies of corresponding vibrations of species E and B₁ or B₂ should nearly be equal so that the ratio of their frequencies should be near to 1. The ratios of the corresponding pairs of vibrations Q1=E¹/B₂¹, Q2=E²/B₁¹, Q3=E³/B₂², Q4=E⁴/B₁²,

$Q5=E^5/B_2^3$, and $Q6=E^6/B_1^3$ are therefore calculated and given in tables I-V. This assignment is caused by the fact, that due to doubling of the unit cell all vibrations will be found as a symmetrical and an asymmetrical vibration of which the asymmetrical one normally is found at higher wavenumbers. As expected the quotients Q1 - Q3 are nearly equal to 1.0, but Q4 - Q6 on the other hand show significant deviations from the ideal value and are found roughly spoken at 0.8, 1.3 and 0.7, respectively.

Lit. Method*	CuAlS ₂			CuGaS ₂								CuInS ₂		CuFeS ₂	
	Ko73	Ko73	And	vdZ	Ko75	Bo77	Bo90	Bo90	Car	Ane	Go92	Go93	Ko75	Bac	Ko75
	Ra/IR	Ra	IR	Ra	Ra/IR	IR	IR	Ra	Ra	Ra	Ra	Ra	Ra/IR	Ra	Ra/IR
A ₁	(315)	315		312	312			312	312	312	312	312	(294)	292	(296)
B ₁ ¹	(443)	-		243	358			-	401	-	358	-	-	-	-
B ₂ ^{1/2}	(268)	268		203	203			240 ⁶	238	203	202	-	-	-	-
B ₃ ¹	(98)	98		138	97			117	116	137	99	97	-	-	-
B _{2-TO} ¹	446	445	456	371	368	362	370	366	367	365	368	-	323	320	360
B _{2-TO} ²	271	266	264	339	262	330	256	262	268	260	258	-	234	-	262
B _{2-TO} ³	(112)	112	105	259	95	256	-	95	95	95	95	-	(79)	75	(90)
B _{2-LO} ¹	498	497	500	402	401	390	400	393	393	399	399	-	352	-	385
B _{2-LO} ²	284	278	285	369	281	346	265	278	288	280	278	-	266	-	272
B _{2-LO} ³	(112)	112	111	284	95	276	-	95	95	95	95	-	(79)	-	(90)
E _{TO} ¹	444	445	452	365	363	366	366	365	367	365	364	-	321	320	357
E _{TO} ²	432	-	430	335	332	344	330	332	332	332	332	-	295	-	322
E _{TO} ³	263	262	228	260	262	250	250	260	273	260	258	-	244	245	263
E _{TO} ⁴	216	218	208	147	156	-	-	166	167	147	165	-	(140)	-	(179)
E _{TO} ⁵	(137)	-	-	95	-	-	-	-	147	-	116	115	(88)	85	(105)
E _{TO} ⁶	(76)	-	-	75	74	-	-	75	75	74	74	74	(67)	65	(72)
E _{LO} ¹	497	494	496	387	384	382	385	386	385	386	387	-	339	-	371
E _{LO} ²	-	-	434	352	352	350	350	352	347	-	348	-	314	-	330
E _{LO} ³	266	265	242	278	276	280	280	277	283	275	271	-	260	-	267
E _{LO} ⁴	217	219	220	167	160	-	-	166	167	184	165	-	(140)	-	(179)
E _{LO} ⁵	(137)	-	-	98	-	-	-	-	147	-	116	115	(88)	-	(105)
E _{LO} ⁶	(76)	-	-	76	74	-	-	75	75	74	74	74	(67)	-	(72)
E ¹ :B ₂ ¹	0.996	1.000	1.009	0.984	0.986	1.011	0.989	0.997	1.000	1.000	0.989	-	0.994	1.000	0.999
E ² :B ₁ ¹	0.975	-	-	1.379	0.927	-	-	-	0.828	-	0.927	-	-	-	-
E ³ :B ₂ ²	0.971	0.985	0.864	0.767	1.000	0.758	0.977	0.992	1.019	1.000	1.000	-	1.043	-	1.019
E ⁴ :B ₁ ²	0.806	0.813	-	0.724	0.769	-	-	0.692	0.702	0.724	0.817	-	-	-	-
E ⁵ :B ₂ ³	1.223	-	-	0.369	-	-	-	-	1.547	-	1.221	-	1.114	1.133	1.167
E ⁶ :B ₁ ³	0.776	-	-	0.544	0.763	-	-	0.641	0.647	0.540	0.747	-	-	-	-
SB ³ #	210	210	(210)	-	192	-	-	212	211	232	194	-	(158)	150	(180)
SE ⁵⁺⁶	213	-	-	170	-	-	-	-	224	222	190	-	155	150	177
DB ³	14	14	-	-	-2	-	-	-22	-21	-42	-4	-	-	-	-
DE ⁵⁻⁶	61	-	-	20	-	-	-	-	72	21	42	-	21	20	33

[†]Ra: Raman data; IR: Infrared data; P: powder data ⁶ extrapolated from spectra of mixed crystals
[#] in the cases where the B₁³ frequency is not observed, 2 B₂³ is given in round brackets

Table I: Vibrational frequencies (in cm⁻¹) of CuAlS₂, CuGaS₂, CuInS₂, and CuFeS₂

From the values in tables I-V it is obvious that corresponding modes of species B₁ and B₂, i.e. those which can be derived from the same sphalerite mode, have nearly the same energy while the corresponding modes of symmetry E, which from symmetry reasons are allowed to couple, split by about 60cm⁻¹ on an average. This splitting varies systematically with the mass difference of the cations: the greater m_A-m_B the greater the splitting. For the pnictides the splitting of the E-modes is normally greater than for the chalcogenides. We therefore introduce the sums SB³ = (B₁³ + B₂³) and SE⁵⁺⁶ = (E⁵ + E⁶) as well as the differences DB³ = (B₂³ - B₁³) and SE⁵⁻⁶ = (E⁵ - E⁶) of the frequencies of modes B₁³ and B₂³ as well as E⁵ and E⁶ as

further criteria for the examination of the literature data, expecting that SB^3 and SE^{5+6} have similar values and that DB^3 , i.e. the splitting of these modes, is small.

Based on these data which describe the similarity of the vibrational spectra of chalcopyrite type compounds, it is now possible to examine the vibrational frequencies given in the literature and their assignment and to identify artefacts and missing frequencies.

The spectra of $CuAlS_2$ recorded by KOSCHEL exhibit ideal E/B ratios and sums and differences patterns (SD pattern), the values given by ANDRIESH on the other hand show some problems, as especially E^3 and E^4 seem a bit too low.

CuAlSe			CuGaSe						CuInSe					CuGaTe			CuInTe			
Lit.	Bo90	And	Rin	Bo77	Bo81	Bo88	Bo90	And	Ram	Go93	Ri78	Neu	Bo88	Rin	Bac	Tan	Ri78	Ri80	Ho81	
method	IR	IR	Ra	IR	PRa	IR	Ra/IR	IR	Ra	Ra	IR	IR	IR	Ra	Ra	Ra	PIR	IR	IR	
A_1			184		188		188		185	183					174	177	178	(136)	(127)	
B_1^1			190		-		-		130	263					-	-	229			
B_2^1			116		(193)		192		110	165				124	-	179				
B_3^1			96		(86)		-		94	76				76	-	67				
B_{2+10}^1	350	370	261	254	249	244	244	257	260	252	212	214	213	215	215	217	209	168	170	
B_{2+10}^2	-	342	-	178	-	186	186	177	202	187	169	181	-	-	-	177	166	154	101	
B_{2+10}^3	-	252	60	-	(86)	-	60	86	68	98	63	64	-	61	65	70	-	-	-	
B_{2+10}^4																				
B_{2+10}^5																				
B_{2+10}^6																				
B_{2+10}^7																				
B_{2+10}^8																				
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B_{2+10}^{89}																				
B_{2+10}^{90}																				

The main problem is, that the modes of symmetry B_1 have not been determined. The same is true for $CuFeS_2$, where only one spectrum given by KOSCHEL and BETTINI is known.

The spectra found in the literature for $CuAlSe_2$, (ANDRIESH et al. and BODNAR et al. (1990)) are not in good agreement. Furthermore Q_5 is much too low for the spectrum of BODNAR et al. (1990) which is probably due to a too high value of the mode B_2^3 . Further investigations are needed.

Spectra of $CuGaSe_2$ are given by BODNAR et al. (1977), BODNAR et al. (1990), BODNAR et al. (1981), BODNAR et al. (1988), RINCON et al., RAMIREZ et al. and q (1993). The data scatter widely and all of them contradict more or less our test criteria.

Lit. method	AgGaS ₂								AgInS ₃		AgGaSe ₂				AgInSe ₂		AgInTe ₂	
	Ho74 IR	Ho74 Ra	vdZ IR	vdZ Ra	Loc Ra	Ko75 Ra	Ko75 Ra/IR	Car Ra	Ko75 PIR	Bo90 IR	vdZ Ra	Mil IR	Ka77 IR	Art IR	Cam Ra	Cam IR	Ka78 IR	Ka78 IR
A ₁	295		295	295	295	295	293	(265)		179					181		(172)	(127)
B ₁ ¹	224		-	334	-	334	-			-					253			
B ₂ ²	160		179	191	180	190	-			-					160			
B ₁ ³	65		118	54	-	54	125			12.5					58			
B ₂ ¹ _{TO}	365	365	365	366	364	367	367	329	325	-	248	246	246	252	250	208	168	
B ₂ ² _{TO}	214	-	216	215	212	212	213	219	210	-	154	148	152	155	155	149	131	
B ₂ ³ _{TO}	-	65	193	193	64	65	65	-	-	-	-	-	-	58	63	41	44	
B ₂ ¹ _{LO}	383	396	400	400	399	399	399	-	-	355	272	269	271	272	275	276	233	181
B ₂ ² _{LO}	244	-	238	239	238	238	215	-	225	-	160	164	159	161	165	161	136	
B ₂ ³ _{LO}	-	65	195	199	64	65	65	-	-	-	-	-	-	58	63	43	44	
E ¹ _{TO}	367	367	368	368	368	368	368	-	329	325	-	250	247	247	251	248	215	173
E ² _{TO}	321	322	323	323	322	325	325	-	289	280	-	208	(244)	-	255	251	200	166
E ³ _{TO}	221	223	223	225	224	226	226	213	219	220	-	159	157	160	162	163	153	130
E ⁴ _{TO}	157	160	157	-	159	157	157	160	-	-	-	133	134	133	137	135	106	-
E ⁵ _{TO}	96	95	90	-	95	95	95	96	-	-	-	79	78	84	79	84	60	42
E ⁶ _{TO}	65	65	-	-	85	34	34	36	-	-	-	-	-	-	27	-	-	-
E ¹ _{LO}	395	394	390	392	391	396	396	392	-	340	276	274	273	275	277	279	231	181
E ² _{LO}	349	334	346	347	346	349	349	-	-	305	238	213	-	-	-	250	212	-
E ³ _{LO}	227	233	230	230	230	232	232	224	-	225	160	163	161	163	165	165	162	138
E ⁴ _{LO}	170	160	160	-	160	160	160	161	-	-	112	139	137	135	138	137	111	-
E ⁵ _{LO}	96	95	93	-	95	95	95	-	-	-	73	-	80	78	84	80	62	43
E ⁶ _{LO}	65	65	-	-	85	34	34	36	-	-	48	-	-	-	-	-	-	-
E ¹ .B ₁ ¹	1.006	1.006	1.008	1.006	1.011	1.003	1.003	-	-	1.000	-	1.008	1.008	1.004	1.012	1.004	1.034	1.030
E ² .B ₁ ¹	-	1.438	-	-	0.964	-	0.973	-	-	-	-	-	-	-	0.992	-	-	-
E ³ .B ₂ ²	1.033	-	1.032	1.047	1.057	1.066	1.066	1.000	-	1.048	-	1.033	1.068	1.053	1.045	1.052	1.027	0.992
E ⁴ .B ₂ ²	-	1.000	-	-	0.833	0.872	0.826	-	-	-	-	-	-	-	0.856	-	-	-
E ⁵ .B ₂ ³	-	1.462	0.466	-	1.484	1.462	1.462	1.462	-	-	-	-	-	-	1.448	1.254	1.463	0.955
E ⁶ .B ₁ ³	-	1.000	-	-	1.574	-	0.630	0.288	-	-	-	-	-	-	0.466	-	-	-
SB ³		130	(386)	311	118	(130)	119	190	-	-	-	-	-	-	116	(126)	(82)	(88)
SE ²⁺⁶	161	160	-	-	180	129	129	-	-	-	-	-	-	-	111	-	-	-
DB ³		0	-	75	10	-	11	-60	-	-	-	-	-	-	0	-	-	-
DE ⁵⁺⁶	31	30	-	-	10	61	61	-	-	-	-	-	-	-	57	-	-	-

Table III: Vibrational frequencies (in cm⁻¹) of AgGaS₂, AgInS₃, AgGaSe₂, AgInSe₂, and AgInTe₂

CuInSe₂ has been investigated by BACEWICZ et al., RINCON et al., BODNAR et al. (1988), GAN et al., RIEDE et al. (1978), NEUMANN et al., and TANINO et al.. The spectrum of TANINO et al. which is complete is not in full agreement with our test criteria. The data of GAN et al. which obviously have been exchanged by mistake for the spectrum of CuGaSe₂ are not included in the table.

Only an infrared powder study has been reported for CuGaTe₂ by RIEDE et al. (1978) which is not complete. Further studies are necessary for this compound. The spectra of CuInTe₂ given by RIEDE et al. (1980) and HOLAH et al. (1981) are not complete as well and need further investigation.

AgGaS₂ has been investigated by KOSCHEL and BETTINI, V. D. ZIEL et al., CARLONE et al., KOSCHEL et al. (1975), HOLAH et al. (1974), and LOCKWOOD and MONTGOMERY. Of these the spectrum presented by KOSCHEL and BETTINI and that of LOCKWOOD and MONTGOMERY are nearly identical with the exception of the mode E⁶. According to our criteria we think that the value given by KOSCHEL and BETTINI is right.

Lit.	ZnSiP ₂						ZnGeP ₂					ZnSnP ₂	ZnSiAs ₂	
	Kam	Att	Ho72	Hum	Deu	Gor	Mi74	Ma74	Be74	Be75	Gor	Kop	Zla69	Ko74
	Ra	Ra	IR	Ra	Ra	Ra	IR	IR	Ra	Ra/IR	Ra/IR	Ra/IR	PIR	Ra/IR
method	Ra	Ra	IR	Ra	Ra	Ra	IR	IR	Ra	Ra/IR	Ra/IR	Ra/IR	PIR	Ra/IR
A ₁	344	335		337	344	337			328	328	328	329		(202)
B ₁ ¹	-	-		-	505	466			389	389	390	-		-
B ₂ ²	-	-		335	351	-			247	247	248	249		(240)
B ₁ ³	131	129		130	131	131			120	120	119	121		-
B ₂ ¹	-	493	491	494	495	494	392	397	396	397	401	401	368	389
B ₂ ² _{TO}	352	359	347	342	356	343	348	342	343	340	338	341	327	242
B ₂ ³ _{TO}	-	-	-	145	145	145	-	-	-	-	-	-	-	-
B ₂ ¹ _{LO}	535	519	509	518	517	518	401	415	-	414	408	411		400
B ₂ ² _{LO}	362	-	360	357	358	361	360	365	-	368	357	361		251
B ₂ ³ _{LO}	-	-	-	145	145	146	-	-	-	-	-	-		-
E ₁ ¹ _{TO}	511	493	500	494	495	494	385	387	386	386	387	387	368	400
E ₂ ² _{TO}	477	464	-	462	463	461	370	366	369	370	369	369	-	-
E ₃ ³ _{TO}	335	328	320	327	337	321	330	327	-	330	328	328	327	233
E ₄ ⁴ _{TO}	270	266	260	264	262	246	202	205	203	203	201	204	-	207
E ₅ ⁵ _{TO}	185	186	185	184	185	185	-	142	141	141	143	143	-	131
E ₆ ⁶ _{TO}	105	102	-	102	102	103	-	-	91	94	96	96	-	-
E ₁ ¹ _{LO}	-	519	516	519	519	518	402	406	406	402	403	405		414
E ₂ ² _{LO}	477	464	-	464	463	464	375	376	375	375	377	377		-
E ₃ ³ _{LO}	335	328	328	-	339	327	332	330	-	332	328	330		337
E ₄ ⁴ _{LO}	270	266	265	-	265	261	204	208	203	203	203	206		211
E ₅ ⁵ _{LO}	185	186	188	187	186	187	-	143	141	141	143	144		133
E ₆ ⁶ _{LO}	105	102	-	-	103	103	-	-	91	94	96	96		-
E ¹ :B ₂ ¹	-	1.000	1.018	1.000	1.000	1.000	0.982	0.975	0.975	0.975	0.965	0.965		1.028
E ² :B ₁ ¹	-	-	-	-	0.916	0.989			0.949	0.951	0.946	-		-
E ³ :B ₂ ²	0.952	0.914	0.922	0.956	0.947	0.936	0.948	0.956	-	0.971	0.970	0.962		0.963
E ⁴ :B ₁ ²	-	-	-	0.788	0.746	-			0.822	0.822	0.811	0.819		0.863
E ⁵ :B ₂ ³	-	-	-	1.269	1.276	1.276	-	-	-	-	-	-		-
E ⁶ :B ₁ ³	0.802	0.791	-	0.785	0.779	0.786			0.758	0.783	0.807	0.793		-
SB ³	(262)	(262)	-	275	276	277			(240)	(240)	(238)	(242)		-
SE ⁵⁻⁶	290	288	-	286	287	288	-	-	232	235	239	239		-
DB ³	-	-	-	15	14	15			-	-	-	-		-
DE ⁵⁻⁶	80	84	-	82	83	82	-	-	50	47	47	47		-

Table IV: Vibrational frequencies (in cm⁻¹) of ZnSiP₂, ZnGeP₂, ZnSnP₂, and ZnSiAs₂

Only infrared spectra are found in the literature for AgInS₂. As well the spectrum given by KOSCHEL et al. (1975) as that of BODNAR et al. (1990) are not complete and therefore cannot be judged by our criteria.

AgGaSe₂ has been investigated by V. D. ZIEL et al., MILLER et al., KANELIS and KAMBAS (1977), ARTUS et al., and CAMASSEL et al. of which the Raman data by CAMASSEL et al. are complete and in good accordance with the test criteria.

The data found in the paper of TYUTEREV et al. seem to be a combination of the frequencies given by V. D. ZIEL et al. and MILLER et al.

The infrared spectra of AgInSe₂ and AgInTe₂ have been published by KANELIS and KAMBAS (1978). While the spectrum of the selenide seems to be reliable there are some problems with the vibrations of low wavenumbers in the case of the telluride.

Lit. method	CdSiP ₂		CdGeP ₂				CdSnP ₂		CdGeAs ₂					
	Be74 Ra/IR	Shi Ra	Be75 Ra	Ma71 IR	Be75 Ra/IR	Ar91 IR	Ar91 IR	Ar91 Ra	Zla71 IR	Irm Ra	Puj Ra/IR	Ho77 IR	Pas IR	Pas Ra
A ₁	326	323	321		321			322		301	196			196
B ₁ ¹	-	-	373		373			377		-	260			260
B ₁ ²	315	314	225		225			228		295	-			165
B ₁ ³	88	87	85		85			88		113	75			75
B ₂ ¹ _{TO}	486	485	391	387	387	399	394	398	-	353	275	270	-	273
B ₂ ² _{TO}	306	297	299	295	295	300	298	295	295	288	206	203	-	205
B ₂ ³ _{TO}	109	108	88	-	88	91	-	91	-	73	73	-	73	73
B ₂ ¹ _{LO}	511	507	398	401	401	410	404	407	354	364	-	278		284
B ₂ ² _{LO}	318	314	-	317	317	317	313	314	-	306	-	210		216
B ₂ ³ _{LO}	109	109	88	-	88	91	-	91	-	73	-	-		73
E ₁ ¹ _{TO}	486	485	385	385	385	381	382	385	339	340	275	272	-	275
E ₁ ² _{TO}	454	449	354	356	354	356	354	358	318	314	259	255	-	259
E ₁ ³ _{TO}	284	286	291	289	289	289	290	295	279	280	206	200	-	203
E ₁ ⁴ _{TO}	252	248	183	179	179	181	181	184	-	146	160	159	-	160
E ₁ ⁵ _{TO}	156	152	121	122	121	119	121	123	-	93	96	95	97	96
E ₁ ⁶ _{TO}	66	66	63	-	63	63	-	64	-	54	46	-	42	46
E ₁ ¹ _{LO}	511	508	402	397	397	401	398	400	354	348	-	280		290
E ₁ ² _{LO}	456	453	364	363	364	369	366	368	327	328	-	258		264
E ₁ ³ _{LO}	290	286	291	293	293	298	295	296	285	283	-	206		209
E ₁ ⁴ _{LO}	256	253	188	181	188	187	183	186	-	147	-	161		165
E ₁ ⁵ _{LO}	160	158	121	124	121	123	122	123	-	94	-	98		97
E ₁ ⁶ _{LO}	66	66	63	-	63	63	-	64	-	54	-	-		48
E ₂ ¹ :B ₁ ¹	1.000	1.000	0.985	0.995	0.995	0.955	0.970	0.967	-	0.963	1.007	1.007		1.007
E ₂ ² :B ₁ ¹	-	-	0.949	-	0.949	-	-	0.950	-	-				0.996
E ₂ ³ :B ₁ ²	0.928	0.963	0.973	0.980	0.980	0.963	0.973	1.000	0.948	0.972	0.985	0.985		0.990
E ₂ ⁴ :B ₁ ²	0.800	0.790	0.813	-	0.796	-	-	0.807	-	0.495				0.970
E ₂ ⁵ :B ₁ ³	1.431	1.407	1.375	-	1.375	1.375	-	1.352	-	1.274	-	-	1.329	1.315
E ₂ ⁶ :B ₁ ³	0.750	0.759	0.741	-	0.741	-	-	0.727	-	0.478				0.613
SB ³	197	195	173	-	173	(182) ^c	-	179	-	186			(146)	148
SE ⁵¹⁶	222	218	184	-	184	182	-	187	-	147	-	-	139	142
DB ³	21	31	3	-	3	-	-	3	-	-40				2
DE ⁵¹⁶	90	86	58	-	58	56	-	59	-	39			55	50

Table V: Literature data of the vibrational frequencies (in cm⁻¹) of CdSiP₂, CdGeP₂, CdSnP₂, and CdGeAs₂.

Of the literature data found for ZnSiP₂ the spectra given by HUMPHREYS, DEUS et al., and GORBAN et al. are similar to each other with the exception of the wavenumbers of the modes B₁¹ and B₁². According to the better agreement with the test criteria we prefer the data given by HUMPHREYS. The data given by KAMINOV et al., ATTORESI et al., and HOLAH (1972) are not complete

Spectra of ZnGeP₂ are found in the literature by GORBAN et al., MILLER et al., MARKOV et al., BETTINI and MILLER, BETTINI, and KOPYTOV and POPLAVNOI. The data of these authors are in good agreement to each other and do not contradict our test criteria. We prefer the spectra of GORBAN et al. and MILLER, but only because they are more complete than those given by the other authors.

ZnSnP₂ has been investigated by infrared measurements on powders only by ZLATKIN et al. (1969). Further investigation on this compound is necessary. The same holds for ZnSiAs₂ which has been measured by PUJOL et al. in both infrared and Raman experiments.

Spectra of CdSiP₂ have been published by BETTINI and BETTINI et al. as well as SHIRAKATA. The spectra are in agreement within the estimated experimental error of the vibrational frequencies. The main difference is that of the mode B₂² which is found at

306 cm^{-1} by BETTINI and at 297 cm^{-1} by SHIRAKATA.

CdGeP_2 has been investigated by BETTINI and MILLER, BETTINI, MARKOV and RESHETNYAK, and ARTUS et al.. These data are also in very good agreement and we prefer the spectra of BETTINI and ARTUS et al. only due to the fact that all vibrations have been observed.

	CuAlS	CuGaS	CuInS	CuAlSe	CuGaSe	CuInSe	CuAlTe	CuGaTe	CuInTe
A_1	315	312	294	191	187	177	138	136	127
B_1	443	358	309	367	264	225	306	220	187
B_2	268	203	162	221	165	129	191	144	114
B_3	98	97	83	87	83	72	75	71	62
B_4	446	368	323	358	249	213	287	200	170
B_5	271	262	234	189	182	174	161	155	151
B_6	112	95	79	95	80	63	84	72	59
E^1	444	363	321	364	252	216	293	202	172
E^2	432	332	295	338	253	209	277	206	170
E^3	263	262	244	186	185	177	158	157	151
E^4	216	165	140	180	141	113	151	119	94
E^5	137	115	88	118	98	74	116	100	75
E^6	76	74	67	61	57	50	48	46	39

	AgAlS	AgGaS	AgInS	AgAlSe	AgGaSe	AgInSe	AgAlTe	AgGaTe	AgInTe
A_1	304	295	282	186	181	172	135	133	127
B_1	422	334	292	349	253	214	292	210	178
B_2	253	190	152	209	160	123	181	138	108
B_3	69	65	57	61	58	50	53	50	44
B_4	448	367	316	359	252	208	286	198	168
B_5	225	212	204	160	155	149	136	130	131
B_6	80	65	52	68	58	41	60	52	44
E^1	450	368	317	368	255	215	296	204	173
E^2	425	325	283	332	251	200	271	200	166
E^3	226	226	214	160	162	153	136	134	130
E^4	205	157	128	174	137	106	147	116	91
E^5	117	95	73	100	84	60	99	84	63
E^6	39	34	32	31	27	25	26	24	21

Table VI: Estimated values of the vibrational frequencies for 18 chalcogenides with chalcopyrite structure based on the reliable literature data (bold characters) in cm^{-1} .

Only two spectra are known for CdSnP_2 . In the IR spectrum published by ZLATKIN et al. (1971) only 4 of the allowed 9 TO modes are observed, the frequencies of which are in fairly good agreement with the data given by IRMER et al.. The spectrum of IRMER et al. on the other hand is nearly complete and matches to the general pattern of the chalcopyrite spectra with the exception of the frequencies of the B_1 – modes, which are obviously too high in comparison with those of CdGeP_2 and with the corresponding modes of species E which is shown by the small values of Q4 and Q6 (see table V).

The data published by PUJOL et al., HOLAH et al. (1977), and PASCUAL et al. (1991) for CdGeAs_2 are in good agreement to each other and also to our test criteria.

The data which we think are reliable, are printed in bold characters in tables I-V. For the spectra of the other chalcopyrite type compounds there are more or less problems due to missing frequencies, wrong assignments, or artefacts.

Tables I-V also compile the frequencies of the LO modes obtained by IR or Raman measurements. As can be seen, the TO-LO splittings scatter widely, but nevertheless some trends are noticed: Both in species B_2 and E it is normally the band with the highest wavenumber, which shows the largest splitting followed by the band with the second highest wavenumber. E^3 exhibits normally a smaller splitting than the corresponding vibration of species B_2 , the B_2^2 , all the other modes show very small TO-LO splittings only.

	ZnSiP ₃	ZnGeP ₃	ZnSnP ₃	ZnSiAs ₃	ZnGeAs ₃	ZnSnAs ₃	ZnSiSb ₃	ZnGeSb ₃	ZnSnSb ₃
A ₁	337	328	309	202	199	187	146	143	134
B ₁ ²	484	389	333	384	275	236	320	229	196
B ₂ ²	335	247	191	240	178	142	206	155	123
B ₃ ³	130	120	106	112	107	93	96	93	80
B ₃ ¹	494	397	350	389	274	236	315	222	189
B ₃ ²	342	340	331	242	238	234	209	205	199
B ₃ ³	145	122	98	118	99	81	102	86	70
E ₁ ¹	494	386	337	400	273	235	322	222	189
E ₂ ³	462	370	321	361	268	228	297	220	185
E ₃ ³	327	330	318	233	235	227	200	202	195
E ₄ ⁴	264	203	157	207	166	131	176	139	111
E ₅ ⁵	184	141	108	131	114	89	131	114	88
E ₆ ⁶	102	94	85	82	76	66	68	62	54

	CdSiP ₃	CdGeP ₃	CdSnP ₃	CdSiAs ₃	CdGeAs ₃	CdSnAs ₃	CdSiSb ₃	CdGeSb ₃	CdSnSb ₃
A ₁	326	322	301	198	196	183	143	140	131
B ₁ ²	462	377	318	366	260	224	305	217	187
B ₂ ²	315	228	179	223	165	133	195	146	117
B ₃ ³	88	88	75	78	75	65	68	64	56
B ₃ ¹	486	398	353	390	273	235	315	221	189
B ₃ ²	306	295	288	211	205	200	180	175	171
B ₃ ³	109	91	73	86	73	58	73	63	51
E ₁ ¹	486	385	340	401	275	236	324	223	191
E ₂ ³	454	358	314	352	259	222	290	215	181
E ₃ ³	284	289	280	202	203	196	174	175	168
E ₄ ⁴	252	184	146	204	160	125	171	135	106
E ₅ ⁵	156	123	93	113	96	74	112	96	74
E ₆ ⁶	66	64	54	49	46	39	39	35	30

Table VII: Estimated values of the vibrational frequencies for 18 pnictides with chalcopyrite structure based on the reliable literature data (bold characters) in cm⁻¹.

Starting from the reliable spectra it is possible to calculate estimated values for the uncertain frequencies by transfer of the spectral pattern. This is done for each frequency of the spectrum by the rule of three and averaging over values obtained from comparing different couples of compounds. In a first step we compare only such pairs of compounds in which the differing ions belong to adjacent periods of the periodic table. To obtain for instance estimated frequencies for AgInS₂ we multiply each of the frequencies of AgGaS₂ by the ratio of the corresponding frequencies of CuInS₂ and CuGaS₂, CdSnP₃ and CdGeP₃ or AgInSe₂ and AgGaSe₂. The mean values of the frequencies obtained by these calculations are given in tables VI and VII. A comparison of these data with the literature data given in tables I – V can be used to sort out those experimental frequencies which are artefacts or wrongly assigned, obviously. These calculated frequencies are especially useful to obtain estimated values for the modes of species B₁, which only in a few cases are observed unambiguously.

Conclusion

Our comparison of the literature data for the vibrational frequencies of chalcopyrite type compounds verifies the assumption that the force constants and the normal coordinates within this group of compounds are similar to a large extent. Therefore the frequency ratios of corresponding modes of species B and E as well as the sum and difference criteria used in this paper are well suited to critically evaluate the data. Based on these criteria 12 chalcopyrites could be singled out for which the spectra seem to be reliable and complete (though in some cases the frequencies of the B₁-modes are still missing) and which could be used in force constant calculations. The results of these calculations will be given in a second and third part of this series of papers for a short range and a rigid ion model, respectively. Furthermore it can be concluded that some more experimental work has to be

done to obtain good and reliable data for the other chalcopyrites. A basis for these experiments could be the compilation of the estimated frequencies given in tables VI and VII. In preliminary experiments of Elitok for instance the A_1 -mode of CuAlSe_2 could be observed for the first time at 185 cm^{-1} very near to the estimated value of 191 cm^{-1} .

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