

Lattice Dynamical Calculations on Compounds Crystallizing in a Thiogallate-Type Structure

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Received December 28, 1993; in revised form May 23, 1994; accepted May 26, 1994

Lattice dynamical calculations for thiogallate-type compounds AGa_2X_4 with $A = Cd$ or Hg , and $X = S$ or Se have been performed on the basis of a short-range force constant model. Discrepancies in the experimental frequencies and crystal structures reported for these compounds in the literature by different groups are discussed with respect to the short-range force constants and potential energy distributions resulting from our calculations. © 1995 Academic Press, Inc.

INTRODUCTION

Recently we reported (1) on the IR reflection spectra of the compounds $CdGa_2S_4$, $CdGa_2Se_4$, $HgGa_2S_4$, and $HgGa_2Se_4$, which crystallize in the thiogallate type (space group $I\bar{4}$), a defect variant of the chalcopyrite lattice.

Force constant calculations for thiogallate-type compounds have already been published by Kerimova *et al.* (2), Tyuterev *et al.* (3), and Gupta (4). These reports are contradictory (i) due to the different sets of frequencies used for the calculations (there are major discrepancies in the literature regarding the experimental frequencies of the lattice modes) and (ii) with respect to the sets of force constants obtained from the calculations.

In this paper we present results of lattice dynamical calculations on the basis of a short-range model using Wilson's GF-matrix method in order to solve the questions pending in the literature.

INFRARED AND RAMAN SPECTRA

The optical phonons of thiogallate-type compounds, especially $CdGa_2S_4$ and $CdGa_2Se_4$, have been investigated by many authors (5-11). According to factor group analysis (12) for $k = 0$,

$$\Gamma = 3A + 5B + 5E,$$

all 13 modes are Raman-active and 10 are IR-active. Not all allowed modes could be measured in all cases. A compilation of the frequencies found in the literature is shown in Table 1.

While the agreement of the frequencies obtained by different authors is good in the case of the modes of species E , there are uncertainties in the frequencies of species A and B . One mode of species B , for instance, has not been observed by some of the authors while others assign a band at 142 or 242 cm^{-1} in the case of $CdGa_2S_4$ and at 76 or 178 cm^{-1} for $CdGa_2Se_4$ to species B .

Similar contradictory results are found for the Raman-active vibrations of species A , of which only the vibrations $A(2)$ and $A(3)$ in Table 1 are without doubt. The vibrations with the highest frequencies are found near 393 or 360 cm^{-1} for $CdGa_2S_4$ and at 266 or 210 cm^{-1} for $CdGa_2Se_4$, if this mode is observed at all. According to MacKinnon (13) the Raman line at 266 cm^{-1} for $CdGa_2Se_4$ is due to a two-phonon absorption. From a comparison with the zone-edge phonons of sphalerite-type compounds he expects the missing A mode near 188 cm^{-1} . Razzetti *et al.* (5) found a weak band at 210 cm^{-1} which, however, has not been observed by any other research group. Finding only two Raman-active vibrations, Park *et al.* (14) inferred that the space group of $CdGa_2Se_4$ is $I\bar{4}2m$ instead of $I\bar{4}$.

POTENTIAL MODEL

As can be seen from the compilation of the vibrational frequencies (see Table 1) the TO/LO splitting of the different modes is relatively small leading to the conclusion that bonding in these compounds is mainly covalent in nature. We therefore decided to do our lattice dynamical calculations on the basis of a short-range force constant model. For the description of the potential energy of the thiogallate lattice in this model we used the following force constants: three valence force constants $K1$, $K2$, and $K3$ for the interaction of the three metal ions occupying different crystallographic sites with their nearest sulfur neighbors (see Fig. 1). Components of the vibrations perpendicular to the valence forces we describe by the three angle deformation force constants $H1$, $H2$, and $H3$. Though the angles around a tetrahedrally coordinated cation are not equal due to the tetragonal distortion of

TABLE I
Infrared (IR) and Raman (R) Spectra of Different Thiogallates

Ref. Mode	CdGa ₂ S ₄							CdGa ₂ Se ₄					HgGa ₂ S ₄			HgGa ₂ S ₄	
	(6) R	(7) R	(8) IR	(2) IR + R	(9) IR	(9) R		Mode	(5) R	(2) IR + R	(9) IR	(10) IR	(11) P	(9) IR	R	(11) P	(9) IR
A1	359	361		369	393			A1	210	266		141			391		
A2	308	311		314	311			A2	188	190		104			316		
A3	218	219		221	219			A3	141	140		68			225		
B1TO	371	370	367	372	366	366	—	B1TO	264	254	259	255	376	369		254	257
B2	291	322	321	323	326	325	322	B2	222	220	225	228	317	323		222	221
B3	253	255	254	254	256	260	259	B3	196	198	197	172	243	253	254	179	179
B4	161	160	160	162	242	243	—	B4	124	176	178	120	157	236		120	162
B5	—	—	—	142	166	165	166	B5	76	112	123	86	—	167	167	—	120
B1LO	394	395	392	396		391		B1LO	280	275	277	275		386			272
B2	310	344	342	344		348		B2	237	232	236	233		343			232
B3	263	268	266	269		268		B3	202	198	201	176		258			184
B4	168	170	170	172		246		B4	128	178	181	125		239			165
B5	—	—	—	148		172		B5	76		125	91		170			123
E1TO	364	362	361	362	364	363	364	E1TO	262	250	253	257	361	365	364	240	251
E2	323	323	319	324	332	325	323	E2	241	236	240	240	—	325	319	—	238
E3	241	242	239	240	240	241	242	E3	178	174	176	172	228	234	237	160	161
E4	136	134	138	135	120	136	135	E4	105	104	102	85	126	132	134	—	101
E5	84	84	84	84	82	84	85	E5	68	68	65	66	59	64	64	52	52
E1LO	387	388	390	390		388		E1LO	278	274	276	276		383			272
E2	354	353	348	354		352	352	E2	249	242	246	248		345	350		245
E3	248	241	245	248		246		E3	183	180	181	180		238			165
E4	141	135	135	140		138		E4	105		103	91		133			101
E5	89	88	88	90		88		E5	70		68	68		68			56

the lattice (see Table 2) we only use one bending constant for each metal–chalcogen tetrahedron. Especially for the description of the Raman-active vibrations of species *A*, where according to the symmetry coordinates (12) only the chalcogenide ions are vibrating, we introduced next nearest, i.e., chalcogenide–chalcogenide, interactions with force constants F_1 , F_2 , and F_3 , where F_1 stands for the X – X distances which are shortened and F_2 for those which become longer by the tetragonal distortion. F_3 describes the X – X interactions in the xy plane of the lattice. A compilation of the different force constants, the corresponding internal coordinates, and the interatomic distances and angles obtained from single crystal structure determinations (15–18) is given in Table 2.

CALCULATIONS

The force constant calculations have been performed with a modified version of Shimanouchi's program LXSM (19). As utilization of the symmetry coordinates given in (12) did not result in a blocking of the dynamical matrix for species *E*, we used complex symmetry coordinates.

Because of the uncertainties concerning the frequencies of the *B* modes, as discussed above, we performed the first step of the calculations on the basis of the TO frequencies given in (9) assuming that the next nearest neighbor interactions are equal, i.e., $F_1 = F_2 = F_3$. To obtain information on the uncertain frequency we did the calculations twice: first with a frequency with zero weight in the fourth position of species *B* and second with a frequency with zero weight in the fifth, i.e., last position. The results of these calculations are given in Table 3 for CdGa₂S₄, in Table 4 for CdGa₂Se₄, and in Table 5 for the mercury compounds. The force constants were varied in order to minimize the function

$$DF = \sqrt{\sum W_i} (FRO_i - FRC_i)^2 / \sum W_i,$$

where FRO_i and FRC_i are the observed and the calculated frequencies and W_i is the corresponding weight. In order not to miss any significant minimum of DF we varied systematically the force constants K_1 , K_2 , and K_3 and adjusted the other force constants so as to minimize DF using $W_i = 0$ for all uncertain frequencies. The result of

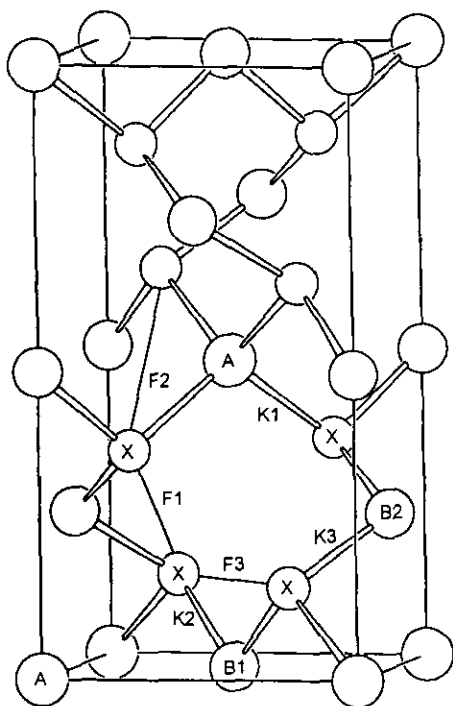


FIG. 1. Unit cell of the thio-gallate lattice showing some of the force constants used in the potential model.

these calculations for CdGa_2S_4 as an example are shown in Fig. 2, where the color of the points symbolizes the value of DF. Light gray indicates relatively high values of DF and black indicates small values. The figure shows that there are at least two different minima, $M1$ and $M2$, in the whole solution set which have nearly the same values of DF. Similar results are obtained for the other compounds under investigation and also for chalcopyrite compounds (20).

In all calculations the best agreement between observed and calculated frequencies, i.e., the smallest value of DF, is observed under the assumption that the uncertain vibration is of the lowest energy (see Table 3, 4, and 6). Further investigation is needed to determine why in some investigations a vibration with a similar frequency as $E(4)$ can be observed. Possible reasons for this finding are the formation of twins or domain crystals, which may have different space groups, induced by the incorporation of iodine into the crystals during the preparation of the crystals by chemical transport reactions.

In the second step we added the modes of species A to our calculations and to avoid the problems with the experimental results as discussed above, we performed two different calculations: (i) the modes of highest energy for CdGa_2S_4 and CdGa_2Se_4 are at 361 and 210 cm^{-1} , respectively; (ii) the third Raman line is to be found between

TABLE 2
Interatomic Distances (pm) and Angles ($^\circ$) and Corresponding Force Constants (FC)
of the Potential Model

Internal Coordinate			CdGa_2S_4		CdGa_2Se_4		HgGa_2S_4	HgGa_2Se_4
FC	N		(15)	(18)	(16)	(18)	(17)	(18)
$K1$	AX	4	243.6	253.8	263.7	257.6	252.9	261.1
$K2$	$B1X$	4	237.3	228.0	241.1	242.8	228.1	240.9
$K3$	$B2X$	4	229.9	227.6	241.6	241.9	228.3	240.3
$H1$	XAX	2	110.4	113.4	110.9	109.8	112.4	110.1
$H1$	XAX	4	109.0	107.5	108.8	109.3	108.0	109.2
$H2$	$XB1X$	2	108.3	104.7	103.3	104.9	103.8	103.2
$H2$	$XB1X$	4	110.1	111.9	112.6	111.8	112.4	112.7
$H3$	$XB2X$	2	120.0	119.3	120.8	119.4	119.4	119.5
$H3$	$XB2X$	4	104.5	104.8	104.1	104.8	104.8	104.7
$F1$	$XX-V$	4	357.4	361.9	367.0	367.9	358.1	367.7
$F1$	$XX-B2$	4	363.6	360.7	381.1	383.2	361.8	380.5
$F2$	$XX-B1$	4	389.0	377.8	401.2	402.2	379.0	401.1
$F2$	$XX-A$	4	396.7	409.4	428.7	420.1	409.3	425.5
$F3$	$XX-B1$	2	384.7	361.0	378.2	385.0	359.1	377.6
$F3$	$XX-V$	2	386.7	395.1	394.1	389.2	387.5	391.5
$F3$	$XX-B2$	2	398.2	392.7	420.0	417.7	394.2	415.2
$F3$	$XX-A$	2	400.2	424.3	434.4	421.6	420.3	427.8

TABLE 3

CdGa₂S₄: Observed (FRQ) (from Ref. (9)) and Calculated (FRC) TO-Frequencies (cm⁻¹), Potential Energy Distribution PED/% and Force Constants (Ncm⁻¹) for the Two Minima M1 and M2 and Two Different Placements of the "Unknown" Frequency

FRQ	M1 B5(4)		M1 B5(5)		M2 B5(4)		M2 B5(5)		
	FRC	PED	FRC	PED	FRC	PED	FRC	PED	
B1	366	373	K2 58 K3 22	368	K2 67 K3 12	360	K1 62 K3 22	367	K1 71 K3 10
B2	326	324	K3 37 K1 25	329	K3 46 K1 28	330	K2 43 K3 24	332	K3 39 K2 37
B3	261	268	K1 50 H1b14	257	K1 30 K3 18	275	K2 27 K3 22	258	K3 27 K2 26
B4	166	(145)	H3a40 H1b26	165	H3a56 H2b10	(141)	H3a34 H1b22	164	H3a60 H1b16
B5	166	144	H1a47 H2a27	(109)	K1 26 H2a24	141	H1a33 H2a28	(123)	H1a43 H3b19
E1	364	363	K2 51 K3 26	359	K2 60 K3 23	361	K1 61 K3 13	363	K1 64 K3 12
E2	325	320	K3 52 K2 22	325	K3 56 K1 18	319	K3 60 K2 19	322	K3 63 K2 17
E3	241	236	K1 61 K2 20	238	K1 60 K2 15	238	K2 60 K1 18	240	K2 63 K1 16
E4	137	146	H1b72 H3b15	138	H2b51 H3b31	142	H1b76 H3b12	138	H1b61 H3b33
E5	85	95	H2b69 H3b27	86	H1b30 H3b17	98	H2b70 H3b27	86	H2b39 H3b23
DF (cm ⁻¹)		9.4		2.8		11.1		2.5	
K1	AX	0.88		0.83		1.44		1.46	
K2	B1X	1.21		1.20		0.82		0.80	
K3	B2X	1.04		1.05		0.97		1.00	
H1	XAX	0.19		0.02		0.18		0.12	
H2	XB1X	0.05		0.08		0.05		0.02	
H3	XB2X	0.05		0.10		0.05		0.11	
F	XX	0.00		0.04		0.00		0.01	

TABLE 4
CdGa₂Se₄ Parameters (See Table 3)

FRQ	M1 B5(4)		M1 B5(5)		M2 B5(4)		M2 B5(5)		
	FRC	PED	FRC	PED	FRC	PED	FRC	PED	
B1	259	263	K2 68 K3 16	261	K2 70 K3 14	258	K1 59 K3 18	256	K1 69 K3 14
B2	225	223	K3 53 K2 20	226	K3 52 K1 18	224	K3 46 K1 26	226	K3 48 K2 17
B3	197	192	K1 54 H1a26	192	K1 56 K3 14	191	K2 51 H2a29	191	K2 52 H2a23
B4	123	(116)	H3a28 H1b28	120	H3a47 H2b20	(131)	H3a48 H2b29	122	H3a49 H2b27
B5	123	115	H1a24 H2a17	(92)	H2a26 K1 18	111	H1a38 H2a24	(99)	H2a28 H1a23
E1	253	258	K3 55 K2 27	257	K3 56 K2 27	261	K3 39 K1 36	258	K1 43 K3 38
E2	240	231	K2 50 K3 30	234	K2 48 K3 29	236	K1 49 K3 41	238	K3 44 K1 43
E3	176	184	K1 54 H1b24	181	K1 80 K2 8	182	K2 47 H2b39	181	K2 57 H2b28

TABLE 4—Continued

FRQ	M1 B5(4)		M1 B5(5)		M2 B5(4)		M2 B5(5)	
	FRC	PED	FRC	PED	FRC	PED	FRC	PED
E4 102	106	H1b54 K1 23	106	H2b48 H3b25	106	H3b43 H2b28	104	H2b38 H3b35
E5 65	70	H2b60 H3b22	66	H1b23 F2b22	74	H1b65 H2b12	66	H1b47 H3b14
DF (cm ⁻¹)	6.1		3.8		6.7		3.6	
K1 AX	0.66		0.78		1.31		1.35	
K2 B1X	0.98		0.93		0.43		0.49	
K3 B2X	0.94		0.93		0.89		0.90	
H1 XAX	0.18		0.01		0.06		0.03	
H2 XB1X	0.04		0.08		0.12		0.10	
H3 XB2X	0.04		0.07		0.09		0.08	
F XX	0.01		0.04		0.00		0.02	

TABLE 5
HgGa₂S₄ and HgGa₂Se₄ Parameters (See Table 3)

HgGa ₂ S ₄						HgGa ₂ Se ₄					
FRQ	M1 B5(5)		M2 B5(5)		FRQ	M1 B5(5)		M2 B5(5)			
	FRC	PED	FRC	PED		FRC	PED	FRC	PED		
B1 369	371	K2 60 K3 24	369	K1 68 K3 11	B1 257	261	K2 71 K3 14	256	K1 69 K3 14		
B2 323	327	K3 39 K1 30	329	K3 44 K2 36	B2 221	223	K3 59 K2 13	223	K3 55 K1 13		
B3 252	250	K1 30 K3 21	248	K2 38 K3 28	B3 179	177	K1 55 H2a16	174	K2 62 H2a21		
B4 167	167	H3a61 H2b11	164	H3a63 H2b15	B4 120	119	H3a49 H2b20	120	H3a51 H2b19		
B5 167	(85)	K1 32 H3b24	(96)	H2a32 H3b29	B5 120	(75)	K1 31 H2a23	(80)	H3b28 H2a26		
E1 365	362	K3 46 K2 40	361	K1 58 K2 18	E1 252	255	K3 52 K2 32	254	K3 44 K1 41		
E2 325	321	K3 36 K2 31	324	K3 61 K1 17	E2 239	232	K2 48 K3 33	233	K1 46 K3 39		
E3 234	231	K1 60 K2 18	233	K2 62 K1 17	E3 161	161	K1 79	164	K2 67 H2b20		
E4 133	133	H2b51 H3b32	136	H2b58 H3b37	E4 101	104	H2b49 H3b24	101	H2b39 H3b33		
E5 64	63	H3b21 H1b15	64	H1b44 H3b22	E5 52	53	F2b23 H3b20	52	F2b23 F1a20		
DF (cm ⁻¹)	2.2		3.1		DF (cm ⁻¹)	3.0		2.9			
K1 AX	0.89		1.62		K1 AX	0.75		1.65			
K2 B1X	1.15		0.74		K2 B1X	0.95		0.43			
K3 B2X	1.15		1.05		K3 B2X	0.91		0.88			
H1 XAX	0.01		0.02		H1 XAX	0.00		0.00			
H2 XB1X	0.07		0.09		H2 XB1X	0.07		0.07			
H3 XB2X	0.12		0.12		H3 XB2X	0.07		0.08			
F XX	0.02		0.00		F XX	0.04		0.04			

TABLE 6
 CdGa₂S₄: Results of the Calculations Including the Raman Data from Ref. (7) (See Table 3)

	FRQ	M1		M1 A2(1)		M2		M2 A2(1)	
		FRC	FRC	FRC	FRC	FRC	FRC	FRC	FRC
A1	361	356	352	—	—	338	360	—	—
A1	312	—	—	317	314	—	—	316	314
A2	312	297	316	(274)	(297)	307	306	(292)	(291)
A3	219	224	222	215	217	231	223	217	219
B1	366	374	369	366	369	381	365	367	367
B2	326	332	323	333	327	329	326	332	333
B3	261	271	251	255	259	263	259	257	256
B4	166	146	166	168	166	155	161	166	168
B5	—	(118)	(90)	(123)	(106)	118	(99)	(118)	(118)
E1	364	356	368	358	361	369	359	360	359
E2	325	316	319	326	323	322	321	324	325
E3	241	244	243	241	240	241	250	239	238
E4	137	150	143	138	138	139	136	138	138
E5	85	94	93	86	84	89	94	85	84
DF (cm ⁻¹)		10.3	5.6	4.0	1.8	9.6	4.9	2.9	3.2
K1	AX	0.87	0.68	0.90	0.86	1.55	1.38	1.42	1.40
K2	B1X	1.20	1.27	1.11	1.23	0.74	0.77	0.76	0.75
K3	B2X	0.90	0.95	1.12	1.01	0.93	0.93	1.00	1.03
H1	XAX	0.18	0.00	0.11	0.01	0.11	0.00	0.11	0.11
H2	XB1X	0.03	0.05	0.01	0.08	0.00	0.05	0.01	0.01
H3	XB2X	0.00	0.09	0.12	0.10	0.08	0.08	0.11	0.11
F1	XX	0.07	0.00	0.02	0.01	0.06	0.00	0.03	0.03
F2	XX	0.07	0.24	0.02	0.07	0.06	0.19	0.03	0.02
F3	XX	0.07	0.06	0.02	0.04	0.06	0.07	0.03	0.03

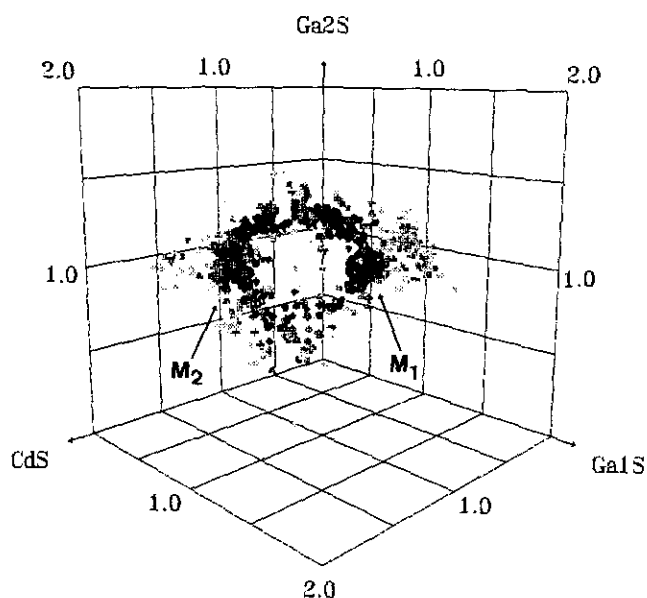


FIG. 2. Solution set for DF for CdGa₂S₄ in the space spanned by the force constants $K_1 \equiv \text{CdS}$, $K_2 \equiv \text{Ga1S}$ and $K_3 \equiv \text{Ga2S}$. The value of DF is symbolized by the color and the density of the points.

the two lines observed in the spectra unequivocally. Again we find the two minima for DF (see Tables 6 and 7), but for both minima the agreement between observed and calculated frequencies is better for case 2, i.e., when the mode of highest energy is at 312 cm⁻¹ for CdGa₂S₄ or at 316 cm⁻¹ for HgGa₂S₄. In the case of the selenium compounds the differences for the two cases are not as significant as in the case of the sulfur compounds, but further calculations with different potential models (20) support the finding of Razzetti *et al.* (5). A calculation on the basis of the whole set of frequencies given in (5) for CdGa₂Se₄ is shown in the last column of Table 7.

DISCUSSION

The results of our calculations lead to the following conclusions with respect to the uncertainties in the spectra of the thiogallates: (i) the uncertain fifth mode of species *B* has the lowest energy in this species. An exact value for the frequency of this mode cannot be given on the basis of these calculations, especially since the wavenumbers and the potential energy distribution of the low-en-

TABLE 7
 CdGa₂Se₄: Results of the Calculations Including the Raman Data from Ref. (5) and for the Whole Raman Data of Ref. (5)
 Including B5(5) (See Table 3)

FRQ	M1		M1A2(1)		M2		M2 A2(1)		M1 (5)	M2
	FRC	FRC	FRC	FRC	FRC	FRC	FRC	FRC	FRC	FRC
A1 210	213	203	—	—	202	208	—	—	204	202
A1 188	—	—	189	188	—	—	195	193		
A2 188	179	190	(178)	(185)	188	189	(183)	(181)	192	185
A3 141	143	146	140	141	144	141	137	140	141	141
B1 259	261	262	260	261	257	259	254	256	267	262
B2 225	227	229	226	226	228	230	228	229	227	226
B3 197	193	197	191	196	191	198	191	193	188	196
B4 123	115	122	119	122	120	121	121	122	122	116
B5 —	(97)	(102)	(91)	(102)	(102)	(102)	(102)	(111)	81	85
E1 253	255	253	257	255	256	257	255	256	260	263
E2 240	231	232	234	233	237	235	237	237	238	240
E3 176	185	175	181	176	179	174	179	177	183	179
E4 102	107	101	105	104	105	100	105	104	106	111
E5 65	74	65	65	65	69	67	65	66	70	74
DF (cm ⁻¹)	6.3	3.9	3.5	2.4	3.9	2.9	4.0	3.0	4.2	4.9
K1 AX	0.73	0.73	0.77	0.74	1.34	1.34	1.30	1.30	0.76	1.39
K2 B1X	0.99	0.93	0.93	0.90	0.62	0.57	0.63	0.61	1.03	0.61
K3 B2X	0.97	0.92	0.94	0.94	0.86	0.91	0.87	0.87	0.95	0.91
H1 XAX	0.12	0.02	0.01	0.02	0.09	0.13	0.10	0.11	0.00	0.14
H2 XB1X	0.02	0.10	0.08	0.10	0.00	0.03	0.00	0.01	0.06	0.02
H3 XB2X	0.00	0.02	0.06	0.04	0.06	0.00	0.06	0.06	0.05	0.00
F1 XX	0.07	0.00	0.05	0.03	0.06	0.04	0.05	0.06	0.02	0.14
F2 XX	0.07	0.08	0.05	0.03	0.06	0.03	0.05	0.00	0.15	0.00
F3 XX	0.07	0.14	0.05	0.09	0.06	0.11	0.05	0.06	0.06	0.03

ergy modes are strongly dependent on the potential model, i.e., which set of force constants is used; (ii) the Raman-active vibrations at 312 and 316 cm⁻¹ for CdGa₂S₄ and HgGa₂S₄, respectively, are those with the highest energy in species A. The Raman lines of higher energy observed in some of the experimental investigations must be of a different origin. The third, missing mode of species A is located between the two vibrations of symmetry A, which have been observed unequivocally.

These conclusions are supported by the fact that for all variations of the potential model, i.e., different sets of force constants, and further variations of the experimental basis, i.e., placement of the "unknown" frequencies, similar results have been obtained (20).

All solutions of our calculations show at least two minima, M1 and M2, with significant differences in the valence force constants. One minimum is always found with $K1 < K2 \approx K3$ and a second with $K1 > K3 > K2$ corresponding to an interpretation of the vibration with highest energy as mainly of A-X or B-X character, respectively.

Both force constant patterns have been described already in the literature on lattice dynamic calculations on thiogallate compounds (see Table 8). Tyuterev *et al.* (3) found a minimum similar to M1 which is reasonable from the fact that they fix $K2 = K3$ and Kerimova *et al.* (2) and Gupta (4) described the vibrational frequencies with force constants corresponding to those of our M2, which is caused by using the modes of highest energy of species A. This choice of experimental frequencies is best described by a large A-X valence force constant and therefore favors a force constant pattern of M2.

Determining which of the two solutions is physically more meaningful requires further information such as can be obtained from a comparison of the spectra of different thiogallate compounds, shown in Table 9. As can be seen from this compilation the first two bands in the absorption spectra are mainly affected by a change of the B cations, while the third band suffers a major shift when the A cations change. This finding can be explained if the force constants K2 and K3 primarily contribute to the potential

TABLE 8
Data of Lattice Dynamics of Thiogallates from the Literature

Mode	CdGa ₂ S ₄ (2)		CdGa ₂ S ₄ (3)		CdGa ₂ S ₄ (4)		CdGa ₂ Se ₄ (2)		CdGa ₂ Se ₄ (3)	
	FRQ	FRC	FRQ	FRC	FRQ	FRC	FRQ	FRC	FRQ	FRC
A1	369	335.7	361	320	393	391	266	231.3	266	180
A2	314	276.8	311	280	312	315	189.9	198.3	189.9	172
A3	221	270.8	219 *	218	219	239	140	156.4	140 *	140
B1	366	359	372	379	372	376	254	266.6	254	251
B2	326	303.4	323 *	324	323	321	220	226.6	220 *	231
B3	256	251.6	254 *	249	254	256	194	197.3	194 *	180
B4	242	160.9	162	116	162	176	176	128.1	112	86
B5	166	119.8	142	92	142	127	112	100.9	75	73
E1	364	352.5	362	380	362	366	250	258.4	250	260
E2	332	290.8	324 *	334	324	305	236	216	236 *	241
E3	240	214	240 *	240	240	230	174	171	174 *	181
E4	120	131.9	135	104	135	153	104	100	104.4	80
E5	82	82.4	84	92	84	91	67.6	59	67.6	63
DF ^a		36		26		11		19		27
DF ^b		34		25		11		18		13
K1	AX	1.428	AX	0.285	AX	1.55	AX	1.39	AX	0.299
K2	B1X	0.628	BX	0.491	B1X	0.60	B1X	0.638	BX	0.365
K3	B2X	0.789	VX ^c	0.088	B2X	0.90	B2X	0.687	VX ^c	0.155
H	—	—	β ^c	0.048	—	—	—	—	β ^c	0.042
F	AB1	-0.054	—	—	AB1	0.10	AB1	-1.06	—	—
F	AB2	0.30	—	—	AB2	0.30	AB2	0.168	—	—
F	B1B2	0.30	—	—	B1B2	0.50	B1B2	0.103	—	—
F	XX	0.074	—	—	XX1 ^d	0.20	XX	0.137	—	—
F	—	—	—	—	XX2 ^d	0.35	—	—	—	—
af ^e	—	—	—	—	XX1 ^e	-0.1	—	—	—	—
af ^e	—	—	—	—	XX2 ^e	-0.1	—	—	—	—
z ^f	—	—	B	0.8	—	—	—	—	B	0.87
z ^f	—	—	X	-0.9	—	—	—	—	X	-0.85

Note. Only the frequencies marked * have been used in the calculations.

^a Error including Raman frequencies.

^b Error only with IR frequencies.

^c VX : Vacancy-X-Force-Constant, β : Keating-Deformation-Force-Constant.

^d XX1 equal to F3, XX2 to F1 and F2 (see Table 2).

^e Angular forces.

^f Charges in units of e.

energy of the first two vibrations and if K1 contributes to the third vibration. The same distribution of the potential energy is found in our calculations for the minimum M1 (see Tables 3–5), where the force constants K2 and K3 have a share of 80% on the potential energy of the first two vibrations of species B and E.

The calculations presented in this paper confirm the relevance of the valence forces to the interpretation of the high energy part of the vibrational spectra. For the description of the low energy part of the spectra, interactions between next nearest neighbors have to be taken into account additionally, in order to describe the long-

range Coulomb forces. This can be done in different ways. For instance a potential model with six force constants, K1, K2, K3, H1 = H2 = H3, F1 = F2 = F3, and F4 (which describes an interaction of the B atoms) gives results similar to those described above, but with F4 = 0.3 N/cm, which is an unreasonably high value for the two Ga atoms in CdGa₂S₄ which are as far apart as 376 pm. This means that the values of the force constants of next nearest neighbor interactions do not represent the Coulomb forces well. Therefore, for an interpretation of these values one has to wait for the results of calculations using a rigid-ion-model (RIM) or polarizable-ion-model

TABLE 9
Infrared Absorption Spectra (cm^{-1}) of Powders from Different Thiogallates (see Refs. 12, 21)

Compound	1		2		3		4		5	
	B	E	B	E	B	E	B	E	B	E
CdAl_2S_4	(453)	(453)	412	425	295	261	206	184	—	94
ZnGa_2S_4	380	371	339	362	281	259	169	136	—	106
CdGa_2S_4	377	364	(320)	(320)	252	236	158	128	—	78
HgGa_2S_4	376	361	(317)	(317)	243	228	157	126	—	59
ZnAl_2Se_4	(383)	(383)	(343)	(343)	221	200	138	126	—	85
CdAl_2Se_4	(380)	(380)	330	342	200	180	132	123	—	69
HgAl_2Se_4	(379)	(379)	326	339	185	165	131	118	—	54
ZnGa_2Se_4	(266)	(266)	(237)	(237)	(201)	(201)	128	—	—	82
CdGa_2Se_4	(259)	(259)	227	244	197	178	122	102	—	68
HgGa_2Se_4	(254)	(254)	222	240	179	160	120	—	—	52

(PIM). The valence force constants K , on the other hand, are not as strongly affected by the Coulomb forces missing in our short range model, though even they will slightly change in RIM or PIM calculations which are in progress.

ACKNOWLEDGMENT

We thank Professor H. C. Gupta, Indian Institute of Technology, Delhi, India, for stimulating discussions during his stay at our laboratory.

REFERENCES

- H. Haeuseler, G. Wäschenbach, and H. D. Lutz, *Phys. Status Solidi B* **129**, 549 (1985).
- T. G. Kerimova, A. Sh. Khidirov, E. Yu. Salaev, and V. Ya. Shteinshtreiber, *Sov. Phys. Solid State Engl. Transl.* **27**, 949 (1985).
- V. G. Tyuterev, S. I. Skachkov, and L. A. Brysneva, *Sov. Phys. Solid State Engl. Transl.* **24**, 1271 (1982).
- H. C. Gupta, *J. Solid State Chem.* **110**, 185 (1994).
- C. Razzetti, P. P. Lottici, and R. Bacewicz, *J. Phys. C: Solid State Phys.* **15**, 5657 (1982).
- P. P. Lottici, A. Parisini, C. Razzetti, and P. Carra, *Solid State Commun.* **51**, 691 (1984).
- Y. Maeyama, Y. Uchihashi, H. Kasahara, K. Yamamoto, and K. Abe, *Jpn. J. Appl. Phys.* **22**, 193 (1983).
- L. M. Suslikov, V. S. Gerasimenko, and V. Yu. Slivka, *Opt. Spektrosk.* **48**, 789 (1980).
- G. Wäschenbach, Dissertation, Universität-GH-Siegen (1984).
- N. N. Syrбу, V. E. Tezlevan, and I. B. Zadnirpu, *Soviet Phys. Semicond. Engl. Transl.* **26**, 1225 (1992).
- C. Razzetti, P. P. Lottici, and G. Antonioli, *Prog. Cryst. Growth Charact.* **15**, 43 (1987).
- H. Haeuseler, *J. Solid State Chem.* **26**, 367 (1978).
- A. MacKinnon, *J. Phys. C: Solid State Phys.* **12**, L655 (1979).
- H. L. Park, H. K. Kim, C. H. Chung, C. D. Kim, T. S. Cho, and W. T. Kim, *Phys. Status Solidi B* **148**, K173 (1988).
- V. Krämer, B. Frick, and D. Siebert, *Z. Kristallogr.* **165**, 151 (1983).
- V. Krämer, D. Siebert, and S. Febbraro, *Z. Kristallogr.* **169**, 283 (1984).
- H. Schwer and V. Krämer, *Z. Kristallogr.* **190**, 103 (1990).
- L. Gastaldi, M. G. Simeone, and S. Viticoli, *Solid State Commun.* **55**, 605 (1985).
- T. Shimamouchi, M. Tsuboi, T. Miyazawa, *J. Chem. Phys.* **35**, 1597 (1961).
- F. W. Ohrendorf, Dissertation, Universität-GH-Siegen (planned for 1994).
- H. Haeuseler, A. Cansiz, *Z. Naturforsch. B* **38**, 311 (1983).