$$\Gamma_{\text{int}} = A_{1g} + A_{2u}$$

$$\Gamma_{\text{ext}}\,(\text{rot}) = A_{1g} + E_u$$

$$\Gamma_{\text{ext}}\,(\text{trans}) = A_{1g} + E_g + A_{2u} + E_u$$

The magnitudes of the observed factor group splitting are 20 and 36 cm^{-1} for $Ca(OH)_2$ and $Mg(OH)_2$, respectively. This large magnitude of splitting could not be explained by Davydov's theory [69] of molecular excitons based on dipole-dipole interactions [70]. Furthermore, it was pointed out that the dipole-dipole interaction would lead to a value of splitting which is opposite in sign to the experimental value [71]. It was shown by Ghosh [71] that the quadrupole-quadrupole interaction together with the dipole-dipole interaction can explain the observed splitting. The value of the quadrupole moment derivative is in agreement with the ab initio value [72, 73].

This feature is common to a few other molecular crystals [73, 74].

C. Metal Dichalcogenides

Among the metal dichalcogenides, MoS_2 occupies a central place. Its importance arises because of the simplicity of its structure and spectra and at the same time its great potential use in material science. Recently, the low temperature properties of TaS_2, $TaSe_2$, and $NbSe_2$ received large attention because of the discovery of the charge density wave properties of these crystals. We present below a discussion of the vibrational spectra of these crystals, particularly with reference to their CDW states in greater detail. Other crystals are reviewed separately.

1. Octahedral Structures

Charge Density Wave States. 1T-TaS_2, 1T-$TaSe_2$. Very recently, vibrational spectra of 1T-TaS_2 and 1T-$TaSe_2$ in commensurate and incommensurate CDW states have been investigated thoroughly [75, 76]. The far-IR reflection spectra of 1T-TaS_2 in the incommensurate and quasicommensurate phases were shown to be featureless. The reflectivity decreases with lowering frequency and it also decreases by 4% on entering the quasicommensurate phase and by 15% on entering the commensurate phase. A number of peaks develop in the commensurate phase at 100 K and 15° incidence. The vibrational modes are found between 50 and 400 cm^{-1}. In the case of 1T-$TaSe_2$, the response from single reflection measurements is so weak that it is difficult to separate the peaks from the background. For this purpose Karecki and Clayman [76] used a dual-cavity technique. In this method a light beam enters a sample-lined cavity through a small hole and makes a number of reflections before reaching the detector [77]. An identical polished brass cavity was used as a reference. The ratio of intensity transmitted through a cavity lined with 1T-$TaSe_2$ to that transmitted through the reference cavity was measured at 4.2, 100, and 295 K. The spectrum at 295 K does not exhibit any sharp feature. There is no strong temperature dependence of frequencies in the commensurate phase. At 100 K a small dip in the reflectivity develops just above the estimated TO frequency of each mode at room temperature. This may arise from strong interaction between free carriers and phonons via collective modes of the CDW's themselves. These dips become very pronounced at 4.2 K, and the observed spectra show as many as 10 sharp peaks. The peaks could not be identified below 50 cm^{-1}. The existence of so many normal modes for the commensurate phase is clear from the fact the super-unit cell contains a larger number of atoms. The acoustic and optic phonon branches ($\underset{\sim}{q} \neq 0$) of the undistorted unit cell is now folded back to $\underset{\sim}{q} = 0$ of the Brillouin zone of the super cell. A smaller Brillouin zone results from the strong CDW distortion of the lattice. A complete group theoretical analysis of these $\underset{\sim}{q} = 0$ modes has not been possible because the space group of the super cell is not known. A table (Table 13) of the observed frequencies of 1T-TaS_2 and 1T-$TaSe_2$ and their ratios can be used to obtain a preliminary knowledge of the atoms involved in these modes. This is based on the fact that the two crystals have identical structures. Thus the high frequency mode ratio is close to the square root of the Se–S mass ratio. Hence the Ta atom is almost at rest for these modes.

Raman scattering studies on 1T-TaS_2 have been reported by Duffey, Kirby, and Coleman [78]. They studied the low temperature commensurate CDW state and observed 12 Raman active modes in the 50-140 cm^{-1} region and 16 Raman active modes in the 220-400 cm^{-1} region. Since they did not analyze the scattered light, all the Raman active modes were observed. The noticeable feature of this measurement is that the Raman peaks in the low frequency region are more intense than those in the high frequency region. They attribute this feature to strong coupling of the phononlike excitations to the crystalline lattice via Coulomb interactions. Hence the CDW states have some distinct roles in the dynamics in addition to the formation of a superlattice.

In the absence of group theoretical analysis, it is difficult to make an exact correlation of the Raman and IR data. However, a comparison of the observed Raman and IR data at low frequency, 50-140 cm^{-1} (Table 12), shows that for each strong far-IR band there is one Raman

TABLE 12

Observed Far Infrared and Raman Frequencies (cm^{-1}) in the Commensurate Charge Density Wave State of 1T-TaS_2 and 1T-$TaSe_2$

1T-TaS_2		1T-$TaSe_2$	
Raman[a]	IR[b]	Raman[c]	IR[b]
56	54	-	45
62	68	-	60
72	78	72	81
80		83	
100	104	99	98
115	107	-	
129			
	204	-	135
	241		153
	256		165
	261		
	286		182
	292		
	306		197
	355		225

[a] Ref. 78.

[b] Refs. 75 and 76.

[c] Ref. 79.

band within 5 cm^{-1}. There is no sharp band in the far-IR corresponding to the 80 cm^{-1} strong Raman peak of 1T-TaS_2 which has been attributed to the coupled CDW phonon excitations as discussed above. A number of pairs of Raman and IR active bands lead to the presence of mutual exclusion rules which would suggest that the unit cell has a center of inversion. In fact, in a super cell having 13 molecular formula units, the highest symmetry possible is that of C_1. This would lead to 57 Raman active modes. Although so many modes were not observed, one should consider the fact that there could be a number of accidental degeneracies when so many modes are packed together in a narrow frequency region in both the Raman and IR spectra. It is clear that all the arguments given above are rather tentative, yet the amount of data obtained from spectroscopic studies would be of great help in elucidating the space group of the commensurate CDW phase.

Temperature-dependent Raman spectra of the CDW state in 1T-$TaSe_2$ have been reported [79]. The Raman spectra were measured at 2, 77, 300, 365, 410, 450, and 480 K using an argon-ion laser. Three modes at 72, 83, and 99 cm^{-1} were found. Again, in this case it is not possible to make correlation between the Raman and IR data (Table 12).

VSe_2 and $TiSe_2$. Besides TaS_2 and $TaSe_2$, charge density wave states have also been studied in octahedral crystals like VSe_2 [80] and $TiSe_2$ [81]. Smith, Tsang, and Shafer obtained the first evidence of CDW formation in 1T-VSe_2. At room temperature they observed one Raman peak at 206 cm^{-1} while at 9 K they observed five sharp Raman lines which could be attributed to superlattice formation. 1T-$TiSe_2$ exhibits CCDW formation at $T_C = 200$ K, below which a superlattice of $2a_0 \times 3c_0$ is formed [81]. There is no evidence of ICDW formation. Above T_C there are only two Raman lines at 134 (E_g) and 195 (A_{1g}) cm^{-1}. Normal incidence reflectivity spectrum shows a single E_u mode at 137 cm^{-1}. The measurement at 53 K yields a few lines in addition to those found in the normal phase. A superlattice $2a_0 \times 3c_0$ has 24 atoms per unit cell. If the space group is D_{3d}^4, the 72 normal modes would be $5A_{1g} + 7A_{2g} + 12E_g + 5A_{1u} + 7A_{2u} + 12E_u$. Only a few of them could be observed. A recent IR measurement by Woo and Brown [82] on $Ti_{1+x}Se_2$ shows a new absorption band at 3500 cm^{-1} which may be interpreted as an excitation across the CDW gap. These measurements are evidence of a superlattice formation with the dimension $2a_0 \times 3c_0$.

Recently, Raman spectra of Ag-intercalated TiS_2 have been reported [83]. In $Ag_{0.3}TiS_2$ at an ambient temperature of 4.2 K, five normal modes were found. Three of these modes at 207, 277 and 311 cm^{-1} were attributed to the formation of a superlattice with $a_0' = \sqrt{3}a_0$, where a_0 is the basal plane lattice parameter of TiS_2. The other modes at 239 and 347 cm^{-1} correspond to their counterparts in the high temperature (300 K) normal lattice. The superlattice formation was also confirmed by electron diffraction measurement [83]. The Ag atoms are ordered at interlayer interstices.

Dichalcogenides of Hafnium, Zirconium, Tin, and Germanium. The other members of the dichalcogenide family having CdI_2-type octahedral lattice, which have received attention of spectroscopists, are HfS_2, $HfSe_2$, SnS_2, $SnSe_2$, ZrS_2, $ZrSe_2$, and $ZrTe_2$. The Raman spectra of most of these crystals were first reported by Smith et al. [84]. Lucovsky et al. [85] also measured the Raman spectra of HfS_2, $HfSe_2$, ZrS_2, and $ZrSe_2$ together with other crystals having the same structure. Group theoretical analysis leads to the modes $A_{1g} + A_{2u} + E_g + E_u$. Hence two Raman active modes A_{1g} and E_g were measured. The observed results conform to that of a typical layerlike lattice and do not exhibit any peculiar feature. These results have already been discussed by Wieting and Verble [9]. In the case of SnS_2 and $SnSe_2$, Smith, Meek, and Liang [86] have recently reported Raman scattering results on different polytypes. SnS_2 has two polytypes 2H and 4H which crystallize with D_{3d}^3 and C_{6v}^4 symmetries, respectively. Recorded Raman spectra for 2H- and 4H-SnS_2 exhibit splitting very similar to that of PbI_2 discussed in Section IV-A-1. The crystal structure of $SnSe_2$ shows the presence of a polytype with three layers per unit cell. However, there is no mode active both in Raman and IR, hence the polytype should have a center of inversion. Thus it is concluded that the polytype is 6H with a D_{3d} factor group and not 6Ha with a C_{3v} factor group.

2. Trigonal Structures

Charge Density Wave States. Similar to 1T-$TaSe_2$, charge density wave states have also been studied in the trigonal prismatic crystals 2H-$TaSe_2$. The crystals possess different structures in the normal phase. 1T-polytypes have a CdI_2-type lattice with one molecule per unit cell, while 2H-polytypes have a MoS_2-type structure with two molecular formula units per unit cell. The Raman spectra of 2H-$TaSe_2$ have been studied by Tsang et al. [79] and Smith, Tsang, and Shafer [80]. The measurements of CCDW phase Raman spectra of 1T-$TaSe_2$ and 2H-$TaSe_2$ [79] show that the temperature dependence of frequencies follows that of the order parameter which is determined from independent measurements. A similar temperature dependence of the observed Raman frequencies of the two polytypes shows that the driving mechanism for CDW instability is the same in both cases.

MoS_2-Type Crystals. As mentioned earlier, MoS_2 has received the largest attention of layer dynamicists. The first detailed measurements were made by Verble and Wieting [87] and Wieting and Verble [8] which were succeeded by a number of other experiments [85, 88-94]. The first-order spectra of MoS_2 published till 1976 have been reviewed [9]. The second-order features observed by Chen and Wang [90] on MoS_2

deserve to be mentioned. Chen and Wang [90] measured the second-order Raman spectra of MoS_2 and recorded the intensity for both s and p-polarizations. In addition to the first-order modes, they observed difference modes, overtones, and second-order optical modes. The intensities of all the second-order modes were much lower than those of the first-order fundamentals. A similar measurement on $NbSe_2$ by Wang and Chen [95] showed that second-order Raman bands have nearly the same intensity as the fundamentals. This shows that the Raman tensor and force field of 2H-$NbSe_2$ is different from that of 2H-MoS_2.

Mead and Irwin [96] measured the long wavelength optical phonons in WSe_2 by first-order Raman scattering. They observed modes at 253 (A_{1g}), 250 (E_{2g}), 178 (E_{1g}), and 25 (E_{2g}) cm^{-1}. The behavior is very similar to that of MoS_2. The interlayer interaction seems to be weaker.

D. Binary Compounds

1. III-VI Compounds

GaS and GaSe. The major interest in this group of compounds has centered around GaS, GaSe, InS, and InSe. Because of earlier controversies regarding the polytype classification of GaSe, there were some doubts regarding the spectral assignments. This ambiguity is now resolved since the most abundant form is now known to be of the ϵ-type. Infrared, Raman, and neutron scattering studies have been carried out for both ϵ- and γ-polytypes of GaSe and β-GaS [97-110]. Most of these results have been reviewed in detail by Wieting and Verble [9]. However, GaSe and GaS continue to be crystals of great importance to spectroscopists, and more recent studies include Davydov splitting, two phonon absorption studies, and theoretical attempts to extract information about the intra- and interlayer forces. Recently the polarization-dependent optical transmission spectra of ϵ-GaSe were measured at room temperature in the frequency region 180-600 cm^{-1} [111]. The observed peaks were interpreted as two-phonon combination modes consisting of both zone-center and zone-boundary phonons. The phonon frequencies at zone boundaries (M point) could be deduced from these two-phonon modes which are active in the infrared. A similar experiment on GaS was also reported earlier [112]. These are indirect measurements of zone boundary phonons by optical methods, which can normally be obtained from neutron inelastic scattering measurements. Considering the simplicity of the experimental techniques, such indirect methods are often useful.

InS and InSe. Very recently Kuroda and Nishina [25, 113-116] published a series of resonance Raman scattering measurements on the semiconducting layer compound InSe which predominantly crystallizes in the γ-polytype with the C_{3v} factor group (Table 1). The mechanism of resonance Raman scattering involves an interaction of vibrational and electronic transitions. When the incident frequency of the laser beam approaches the energy of the A-exciton, the Raman scattering efficiency increases rapidly. An A-exciton is formed by an electron of the lowest conduction band and a hole of the A-valence band. They observed near resonance spectra with 5145 and 4880 Å lines of the Ar-ion laser at 300 and 77 K, respectively. They found new lines due to single and multimodes of LO phonons. Resonance Raman experiments performed on polar optical phonons in γ-InSe show that the two-phonon scattering spectrum spreads over the frequency range of 50 cm^{-1} with an extremely asymmetric lineshape [113]. This result is explained in terms of 2LO and LO + TO scatterings. The unusual lineshape shows directional dispersion. Further studies of Raman scattering efficiencies by Kuroda and Nishina [114] show anisotropic behavior with respect to the direction of propagation. This arises from the anisotropy of the translational effective mass of the exciton. From an analysis of the exciton-photon scattering process, they obtained the effective masses of electrons and holes. Another resonant Raman scattering measurement of InSe [116] for the in-plane (E modes) phonons at 1.8 and 77 K showed a weak resonance enhancement and could be explained in terms of the two-exciton process where the A and C excitons simultaneously serve as the resonance intermediate states [116]. This phenomenon is peculiar to layered materials. In the case of out-of-plane (A_1 mode) phonons the enhancement is strong and can be explained by a one-exciton process. They also propose a selection rule whereby the A_1 modes can induce only intraband scattering and the E modes can induce only interband scatterings. Kuroda, Munakata, and Nishina [115] performed polarization-dependent resonance Raman scattering by LO phonons and determined the interband optical selection rule. They used a laser beam resonating with the A-exciton edge in γ-InSe. Raman scattering appeared from the crystal surface cut normal to the basal plane only in the $E_i \parallel E_s \perp C$ configuration and not in the $E_i \parallel E_s \parallel C$ one. Since the interaction Hamiltonian is diagonal with respect to polarization of the initial and final exciton states, the dipolar transition to create an A-exciton is allowed only for $E \perp C$ and forbidden for $E \parallel C$. The observed Raman tensor for the E-mode LO phonon is contrary to what is expected from the C_{3v} point symmetry of this crystal. This indicates that the Raman scattering by LO phonons is dominated by Fröhlich interaction [117] of LO phonons with excitons. The interaction

Hamiltonian involves a term $\underset{\sim}{q} \cdot \underset{\sim}{Q}$, where $\underset{\sim}{q}$ is the wave vector of the phonon in the lowest order and $\underset{\sim}{Q}$ is the normal coordinate of the phonon. Since $\underset{\sim}{q}$ is parallel to $\underset{\sim}{Q}$ for an LO phonon, $\underset{\sim}{q} \cdot \underset{\sim}{Q}$ is nonzero and is invariant under any symmetry operation.

A Raman scattering experiment by the same group [26] exhibits pressure-induced layer-to-nonlayer transformation of InSe crystal which is consistent with their X-ray studies [118].

Recently Gasanly and co-workers performed Raman and IR studies of InS and InSe crystals [119-121]. As discussed earlier, InS is not, strictly speaking, a layer crystal. Yet the Raman spectrum of InS has a doublet nature typical for layer crystals. The normal modes at $q = 0$ for InS with the D_{2h} factor group are $4A_g + 4B_{1g} + 2B_{2g} + 2B_{3g} + 2A_u + 2B_{1u} + 4B_{2u} + 4B_{3u}$. GaTe crystallizes with the C_{2h} factor group and has three layers per crystal unit cell [122]. The normal modes are $12A_g + 6B_g + 6A_u + 12B_u$. Raman and IR spectra of GaTe crystals were also reported by many authors [123-126]. Infrared reflectivity measurements of GaTe revealed LO-TO splitting [122]. All the recent measurements have been summarized in Ref. 122. A pressure-dependent Raman scattering measurement [126] of InS exhibits a $D_{2h}{}^{12} \rightarrow D_{4h}{}^{17}$ structural phase transition.

2. IV-VI Compounds

The recent interest on IV-VI layer compounds is mainly on SnS, SnSe, GeS, and GeSe. IR and Raman spectra have been reported by

TABLE 13

Vibrational Frequencies (cm^{-1}) and Davydov Splitting in SnS and SnSe[a]

	A_g	B_{1u}	B_{3g}	B_{2u}	B_{2g}	B_{3u}
SnS	218	222	164	145	290	220
	192	178			160	188
	95	99			85	69
SnSe	151	150			108	96
	130	123				
	71	80				

[a] Ref. 130.

Haas and Corbey [127], Chamberlain, Sirbegovic, and Nikolic [128], Nikolic et al. [129], and Chandrasekhar et al. [130]. The layer factor group for these crystals is C_{2v} (DG 32) while the crystal factor group is D_{2h}. The normal modes for the layer are $4A_1 + 2B_2 + 4B_1 + 2B_2$. A recording of the Raman and IR spectra [130] on SnS and SnSe shows Davydov splitting in these crystals. These results, reproduced in Table 13, show that the splitting is small except in the case of the B_{2g}-B_{3u} pair. In this case the assignment of the Raman modes is not completely unambiguous. It may be mentioned that the vibrational frequencies reported in Ref. 130 do not agree with those in Ref. 129.

Raman and IR spectra of GeSe have been studied by Chandrasekhar and Zwick [131] and Siapkas, Kyriakos, and Economou [132]. The vibrational spectra of GeS have also been studied by Raman [133] and IR [134] methods. Pressure-dependent Raman spectra of GeS and GeSe have been reported by Chandrasekhar, Humphreys, and Cardona [135].

E. Orpiment Structures

Very thorough experimental work on layer dynamics has been carried out by Zallen, Slade, and Ward [7] on the low symmetry crystals As_2S_3 and As_2Se_3 which have a very complicated Raman and IR spectrum because of a large number (20) of atoms within a crystal unit cell [7, 136, 137]. They consistently advocated the use of the diperiodic group in analysis of the layer symmetry modes. In fact, this is really useful for a crystal with low symmetry and, in this respect, orpiment structures have distinct properties compared to other layer structures. The factor group analysis of the diperiodic group of layer and the triperiodic group of the crystal (Section III-B-2) exhibits the identity of layer and includes Davydov splitting of intralayer modes.

Zallen, Slade, and Ward [7] carried out far-IR reflectivity and transmission measurements and Raman scattering to obtain polariton dispersion curves, dielectric dispersion properties, LO-TO splitting, and Davydov splitting. From the dielectric dispersion analysis they obtained the phonon and interband contribution to the dielectric constant. These contributions are nearly the same for the two crystals. They also studied the polariton or coupled photon-phonon dispersion curves, showing the dependence of frequency on the real and imaginary parts of the complex propagation vector $\underset{\sim}{q} = \underset{\sim}{q}_1 + i\underset{\sim}{q}_2$. The difference between the $\underset{\sim}{q} = 0$ and $\underset{\sim}{q} \to \infty$ intercepts of these curves for zero damping gives the LO-TO splitting. The measured TO frequencies and the LO-TO splitting obtained from the polariton dispersion curves are presented in Table 14.

TABLE 14

TO Frequencies and LO-TO Splitting (cm^{-1}) of As_2S_3 and As_2Se_3[a]

	As_2S_3		As_2Se_3	
	TO	LO-TO	TO	LO-TO
E ∥ C	383	3	248	2
	354	9	217	15
	311	13	132	4
	198	7	105	3
	159	7	94	3
	140	8		
E ∥ a	375	3	249	0
	345	4	224	14
	299	28	201	8
	181	4	132	2
			106	2

[a] Ref. 7.

The combined Raman and IR studies on the same specimen of single crystals have resulted in an unequivocal assignment of the A_g-B_u pairs and the resultant Davydov splitting. The frequencies of A_g-B_u pairs obtained from a splitting of A_1-symmetry layer vibrations are collected in Table 15. The splitting, in some cases, is as large as 6 cm^{-1}. They also derived a scaling relation $\bar{\nu}(As_2Se_3)/\bar{\nu}(As_2S_3)$ which is surprisingly constant for all the modes. Hence the frequencies are dominated more by masses than by the vibrational eigenvectors.

The vibrational spectra of As_2S_3 were also investigated later by Zallen [138], Treacy and Taylor [139], DeFonzo and Tave [140], Razetti and Lottici [141], and Besson, Cernagora, and Zallen [142].

The recent study of the effect of hydrostatic pressure on the optical absorption edge and the Raman scattering spectrum of the crystalline orpiment As_2S_3 by Besson, Cernagora, and Zallen [142] reveals interesting information about the layer dynamics. When the pressure is zero, the spectrum is dominated by the diperiodic layer symmetry. The interlayer gap is large and the coupling is small. Hence, in the limit of weak coupling, the vibrational modes in different layers of the 3-dimensional crystal unit do not interact strongly, which results in a set of nearly degenerate modes. The eigenvectors corresponding to different frequencies of the same degenerate mode still depend on the crystal symmetry, although the observed spectrum cannot distinguish them. When pressure is applied on the crystal, it first acts on the weak interlayer gap, so that the layers come closer and the effect of coupling of different layers is felt more strongly. This cross-talking of layers increases with an increase of pressure and at 100 kbar the spectrum is mostly dominated by the crystal symmetry. A remarkable effect of the high pressure is that the two rigid layer modes at 25 and 36 cm^{-1} are both increased to about 60 cm^{-1} at 80 kbar. The doubling of frequency means that the interlayer force is increased four times. Another noticeable effect is that the two frequencies approach each other; this shows a decrease in bonding anisotropy. The compressional and shear modes have nearly the same frequencies because the existence of isolated layer is in question and the idea of defining the compressional and shear modes should be done away with.

The other effect of high pressure would be increased Davydov splitting. In a crystal with a center of symmetry this can be studied only by combined Raman and IR methods. Hence the pressure-dependent Raman study alone does not reveal this information. However, the Raman study of intralayer bond-stretching modes shows that a set of nearly degenerate frequencies around 360 cm^{-1} at $P = 0$ is split apart at higher

TABLE 15

Davydov Splitting A_g-B_u (layer symmetry A_1) of As_2S_3 and As_2Se_3[a]

As_2S_3		As_2Se_3	
(A_g)	$(A_g)-(B_u)$	(A_g)	$(A_g)-(B_u)$
382	-1	273	5
355	1	248	0
311	0	216	-1
204	6	132	0
154	-5	104	-1
136	-4	90	-4

[a] Ref. 7.

TABLE 16

Pressure Dependence of Raman Active Modes in the 360 cm^{-1} Region of As_2S_3[a]

P = 0[b]	P = 28 kbar[c]	P = 45 kbar[c]	P = 61 kbar[c]
357.5	352	349	348.5
360	361	363	366.5
362	366.5	370	376

[a] Ref. 142.

[b] T = 15 K, the 362 cm^{-1} line at P = 0 is not the same as the 376 cm^{-1} line at 61 kbar [142].

[c] T = 300 K.

pressure (Table 16). Since the modes are all Raman active, they are not Davydov components. At high pressure the effect of crystalline environment is strong and there is more mixing of the like symmetry modes to form a resultant normal mode. This will force the energy levels apart, and the result is enhanced separation. The P = 0 measurements were carried out at low temperature, hence the splitting obtained in such case is produced by line narrowing while the magnitude of splitting remains constant. The high pressure data were taken at high temperature, hence there is no line narrowing effect. The observed splitting is because of increased splitting at higher pressure. Similarly, at 25 kbar two like symmetry modes at 145 cm^{-1} repel each other and the crossover is forbidden by the same crystal symmetry. Thus two frequencies of the same symmetry which approach each other at high pressure cannot cross.

F. Ternary Compounds

Very recently, vibrational spectra of a few ternary compounds, $TlGaTe_2$, $TlInTe_2$, $TlInSe_2$, $TlGaS_2$, $TlGaSe_2$, and $TlInS_2$, have been reported [143-149]. Among these crystals $TlGaTe_2$, $TlInTe_2$ and $TlInSe_2$ crystallize in a tetragonal cell with D_{4h}^{18} space group. The primitive cell contains two formula units. In spite of having high symmetry of the factor group D_{4h}, the crystal structure is very complicated and group theoretical analysis predicts the symmetry modes:

$\Gamma = A_{1g} + 2A_{2g} + B_{1g} + 2B_{2g} + 3E_g + B_{1u} + 3A_{2u} + 4E_u$ [148]. The observed IR and Raman spectra conform to the symmetry mode analysis. Normal coordinates, effective ionic charges, and force constants have been determined from the IR spectra [148]. There is some controversy regarding the crystal structure of $TlGaS_2$-type crystals $TlGaS_2$, $TlGaSe_2$, and $TlInS_2$ [149]. The earlier studies [150-153] predicted the space group to be either C_2^2 or C_{2h}^2. However, the later works [154, 155] show that the space group is C_s^4 or C_{2h}^6. The space group C_s^4 would lead to a crystal unit cell with two layers, each containing eight formula units. This would lead to a very large number of optically active modes. The observed result does not agree with this. In the case of the C_{2h}^6 space group, the predicted number of normal modes is also large compared to the observation. Hence the observed Raman [143] and IR [149] spectra of these crystals could not be unambiguously assigned to the symmetry mode. It appears that more systematic investigations are necessary.

V. LAYER DYNAMICS CALCULATIONS

The layer dynamics calculations are mainly aimed at translating the observed vibrational frequencies into a set of parameters that can define a reliable potential function for intra- and interlayer interactions. Theoretical interests on layer crystals are mostly confined to high symmetry crystals. The main reason behind this is the complexity of low symmetry layer crystals (e.g., orpiment) and the fact that most of the familiar layer crystals have high symmetry. Excepting orpiment and a few ternary compounds, all the layer crystals discussed in this article are such that each atomic sheet contributes only one atom to the unit cell (layer or crystal). Since the atoms in different unit cells move in phase at $\underset{\sim}{q} = 0$, the dynamics of atoms at $\underset{\sim}{q} = 0$ can be represented by the dynamics of the complete atomic sheet to which it belongs. In such a case, normal mode eigenvectors can be directly determined by symmetry.

If $\underset{\sim}{k}$ forms an N-dimensional basis set containing unit vectors all oriented in directions perpendicular to the layers and $\underset{\sim}{z}$ is an N-dimensional column vector, the elements of which are displacements perpendicular to the layers, then the displacement for modes perpendicular to the layers will be $\underset{\sim}{k} \cdot \underset{\sim}{z}$; N is the number of atomic sheets per unit cell. These modes are called compressional modes in which the atomic sheets move rigidly against each other. Similarly if $\underset{\sim}{i}$ forms a 2N-dimensional basis set defined by unit vectors oriented in two mutually perpendicular directions along the plane of the layer and $\underset{\sim}{w}$ is a 2N-dimensional column vector, the elements of which are the displacements along the plane of the layer in directions specified by the components of $\underset{\sim}{i}$, then $\underset{\sim}{i} \cdot \underset{\sim}{w}$ denote shear displacements. These modes correspond to rigid sliding of the planes over each other. In case of mass-weighted cartesian coordinates $\underset{\sim}{Z}$ and $\underset{\sim}{W}$, the displacement will be $\underset{\sim}{K} \cdot \underset{\sim}{Z}$ and $\underset{\sim}{J} \cdot \underset{\sim}{W}$, where $\underset{\sim}{K}$ and $\underset{\sim}{J}$ are the mass-weighted basis sets for the compressional and shear modes, respectively. The potential function can be defined in terms of internal coordinates

$$r_i^{\,c} = \sum_{j=1}^{N} A_{ij} z_j \quad \text{and} \quad r_i^{\,s} = \sum_{j=1}^{2N} B_{ij} w_j \tag{5}$$

as

$$2V = \sum_{ij=1}^{N} r_i^{\,c} f_{ij}^{\,c} r_j^{\,c} + \sum_{ij=1}^{2N} r_i^{\,s} f_{ij}^{\,s} r_j^{\,s} \tag{6}$$

In terms of mass-weighted Cartesian coordinates, we get

$$2V = \sum_{i,j=1}^{N} Z_i L_{ij} Z_j + \sum_{i,j=1}^{2N} W_i M_{ij} W_j \tag{7}$$

where

$$L_{ij} = \sum_{k,\ell} \frac{A_{ki} f_{k\ell}^{\,c} A_{\ell j}}{\sqrt{m_k m_\ell}} \tag{8}$$

and

$$M_{ij} = \sum_{k,\ell} \frac{B_{ki} f_{k\ell}^{\,s} B_{\ell j}}{\sqrt{m_k m_\ell}} \tag{9}$$

In principle, the two matrices L and M may be separately diagonalized to obtain the eigenfrequencies. The diagonalization procedure corresponds to setting up a new basis vector, the elements of which are linear combinations of the elements of the old basis vectors $\underset{\sim}{Z}$ and $\underset{\sim}{W}$ for the compressional and shear modes, respectively. Instead of using this brute force diagonalization technique, one can exploit the symmetry and use projection operator technique [13] such that one defines symmetry-adapted basis sets

$$\gamma^{C} = \underset{\sim}{K}\hat{R} \quad \text{and} \quad \gamma^{S} = \underset{\sim}{I}\hat{T} \tag{10a}$$

where $\hat{R}$ and $\hat{T}$ are the projection operators for the compressional and shear motions. In case of shear vibrations, the transformation to symmetry-adapted basis vectors will combine only those vectors which are oriented in one particular direction in the plane of the layer. The corresponding symmetry coordinates may be defined as

$$\underset{\sim}{S}^{c} = \hat{R}^{\dagger}\underset{\sim}{Z} \quad \text{and} \quad \underset{\sim}{S}^{s} = \hat{T}^{\dagger}\underset{\sim}{W} \tag{10b}$$

$\underset{\sim}{S}^{c}$ is N-dimensional and represents N nondegenerate modes perpendicular to the plane of the layer including the acoustic one; $\underset{\sim}{S}^{s}$ is 2N-dimensional and accommodates N pairs of degenerate vibrations in the two mutually perpendicular directions in the plane of the layers including one pair of degenerate acoustic modes. The potential energy now becomes

$$2V = \sum_{i,j} S_i{}^{c} F_{ij}{}^{c} S_j{}^{c} + \sum_{i,j} S_i{}^{s} F_{ij}{}^{s} S_j{}^{s} \tag{11}$$

where

$$F_{ij}{}^{c} = \sum_{k,\ell} R_{ki} L_{k\ell} R_{\ell j} \tag{12}$$

and

$$F_{ij}{}^{s} = \sum_{k,\ell} T_{ki} M_{k\ell} T_{\ell j} \tag{13}$$

The symmetrized force constant matrices $F_{ij}{}^{c}$ and $F_{ij}{}^{s}$ are block diagonalized.

The above choice of internal coordinates and potential function (Eqs. 5 and 6) utilizes force constants f^{s} and f^{c} for the motion of atomic planes parallel or perpendicular to the layers. This choice has some advantages and disadvantages. In the case of high symmetry crystals containing one atom of each atomic sheet in a unit cell, the projection operators $\hat{R}$ and $\hat{T}$ are identical (T contains two identical blocks defining the pair of degenerate coordinates). Thus there is a one-to-one correspondence between a nondegenerate compressional and a degenerate shear motion [156]. If we limit the force field parameters to the same number of nearest neighbors for both motions, the symmetrized force field matrices F^{c} and F^{s} are similar. This will lead to a set of analogous equations for both compressional and shear motion frequencies which will differ only in the numerical values of the respective force constants. This type of method has been used by Wieting [157] for MoS_2 and GaSe, Ghosh [52] for $CdCl_2$-type crystals, Lucazeau [158] for GaS, Anderson and Todoeschuck [53] for $FeCl_2$ and $CoCl_2$, and Sears, Klein, and Morrison [47] for PbI_2. Recently, it has been pointed out [159, 160] that the factor group analysis carried out for $q = 0$ (zone center) may be extended to $q = \pi/C$ (zone boundary), where the two neighboring unit cells move out-of-phase. Hence the treatment is equivalent to using a supercell containing two unit cells so that the zone-boundary modes of a unit cell collapse to the zone center of the supercell which has a smaller Brillouin zone. This has the advantage that the zone boundary modes include the interlayer forces in addition to the intralayer ones. This is particularly useful for crystal polytypes having a single layer per unit cell where the zone-center frequencies are independent of interlayer forces. In the above treatment both the zone-center and zone-boundary frequencies can be expressed analytically. These expressions have been derived for two families of layer crystals which have XAX- or XAAX-type layers [160]. It is apparent from our earlier discussions that almost all the high symmetry layer crystals for which experimental data are known belong to one of these two categories. These expressions are very general and do not depend on the stacking difference or crystal space group. The model of compression-shear type forces is, of course, obtained by sacrificing the knowledge of atomic distribution within a sheet, e.g., it does not recognize the difference between the atomic distribution in atomic planes of MoS_2 and PbI_2 crystals. This is a disadvantage for the compression-shear force constant model which does not contain any knowledge of atom-atom band forces. Furthermore, it has been recently pointed out by Altshul, Bashenov, and Baumann [161] that this type of model is not rotationally invariant. Nevertheless, "the simplicity of the model makes it attractive to use," as stated by Sears, Klein, and Morrison [47].

The first lattice dynamics calculation for layer crystals was carried out by Bromley [162] with a central force model for MoS_2. Wakabayashi, Smith, and Nicklow [91] calculated the phonon dispersion curve of MoS_2 by using a valence force field for strong covalent interaction and an axially symmetric force field for weak interlayer interaction. With the help of seven adjustable parameters they could match the dispersion curve obtained from their neutron inelastic scattering measurement. Their results showed discrepancies for large wave vectors which could not be removed by using a shell model with polarizable Mo. Jandl, Brebner, and Powell [109] analyzed their neutron scattering data on GaSe by means of a simple axially symmetric Borr-von Karman force constant model. Zallen and Slade [46] utilized a 3-parameter valence force field model to obtain the stiffness of the lead-iodine covalent bond and the iodine-iodine interlayer bond in PbI_2. They could reproduce the Davydov splitting in 4H-PbI_2. Lucovsky and White [39] have shown that a central force model can account for the observed anisotropy of Raman modes in PbI_2, but cannot explain the IR modes. They also used a valence force field model including noncentral three-body interactions, but this model cannot explain the large splitting of the IR modes. Van der Valk and Haas [163] have shown that the large anisotropy of the optical modes in PbI_2 is due to long-range dipolar interactions. Recently, Maiti and Ghosh [164] have proposed a simple atom-atom force constant model where factor group analysis is carried out for the normal modes and the frequencies are expressed in terms of the force constants and geometric parameters. This model is rotationally invariant. It has also been extended to the two-layer unit cell of 2H-MoS_2 [165]. In order to take account of distant neighbor interactions, one has to define analytic potential functions for these interactions. For this purpose, one must take care of the equilibrium conditions of the lattice such that the macroscopic crystal must be invariant with respect to the rigid body translation and rotation. These conditions, derived by Boyer and Hardy [166], have been used by Ghosh and Maiti [167] to explain the vibrational data of 2H-MoS_2 by means of an exp-6 potential function for interlayer interaction.

The lattice dynamics of comparatively more ionic crystals of $CdCl_2$ or CdI_2 structures have been studied by the shell model by Pasternak [168], Frey and Zeyher [169], and Benedek and Frey [50]. Pasternak [168] used a static-displacement shell model introduced by Cran and Sangster [170]. He fitted the acoustic dispersion curves of $FeCl_2$ measured by Yelon, Scherm, and Vettier [171] and also used the optical frequencies of $MnCl_2$ and $CoCl_2$ by Lockwood [58]. Frey and Zeyher [169] used an extended shell model for PbI_2 including both static and dynamically induced electronic dipoles. They demonstrated the importance of static dipoles at the iodine ions on the observed spectroscopic features. Benedek and Frey [50] have performed a detailed extended shell model calculation for dichlorides and dibromides of V, Mn, Fe, Co, and Ni. The results are in agreement with available neutron scattering data.

VI. SUMMARY

We have attempted to highlight the dynamical properties of layer crystals, particularly from the point of view of their layerlike nature. The very weak nature of interlayer forces apportions a special property to these crystals. The methods of factor group analysis, widely used for molecular crystals, can be easily extended to both the individual layer and the crystals. The layer crystals, having relatively simple crystal structures, can be classified on the basis of their symmetry properties. Group theoretical analysis for almost all known examples of layer crystals have been included in this review. In addition to the fact that these results can be easily applied to simple polytypes, they can also be extended to higher polytypes and relatively complicated examples.

In the section on experimental observations we have summarized the recent studies on vibrational spectra of layer crystals. Special emphasis has been laid on the charge density wave states originating from the formation of supercells, two-phonon processes, etc. Many of these studies are the products of "the renaissance period" in the history of spectroscopy engineered by the discovery of laser. The vast amount of data collected in the literature and their attempted interpretations show that many things still remain to be understood. One has to wait until more and more data are obtained from other types of experiments on the structure of supercells. Theoretical works on these crystals are also of an elementary type, chiefly motivated to provide interpretation of experimental data.

In this article we have included pure crystals. However, a large number of mixed crystals like $AX_{2-n}Y_n$ or $AX_{1-n}Y_n$ have also been studied to obtain information about the host-guest interactions, stacking faults, defects, etc. [101, 172]. A large number of intercalation compounds have also been studied. The most important of these are the intercalated chalcogenide compounds which form superconductors at high temperatures [173]. Very recently Raman and IR investigations have been reported on intercalated pristine compounds [174]. Results of all these studies would add a new dimension to the physics of layer crystals. These studies are outside the scope of the present work.

In summary, we conclude that the experimental data on vibrational spectroscopy have always supplemented the crystallographic data obtained by X-ray or neutron scattering techniques. The combination of these two types of studies has led to the discovery of new phases of crystals as well as having paved the way for understanding the nature of atom-atom interactions in crystals.

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REFERENCES

[1] W. W. Coblentz, Phys. Rev., 26, 252 (1905).

[2] E. K. Plyler, Ibid., 28, 284 (1926).

[3] H. M. Randall and H. H. Nielsen, Ibid., 31, 1131 (1928).

[4] R. T. Mara and G. B. B. M. Sutherland, J. Opt. Soc. Am., 43, 1100 (1953).

[5] D. Krishnamurthy, Proc. Indian Acad. Sci., A50, 223 (1959).

[6] S. S. Mitra, Solid State Phys., 13, 1 (1962).

[7] R. Zallen, M. L. Slade, and A. T. Ward, Phys. Rev. B, 3, 4257 (1971).

[8] T. J. Wieting and J. L. Verble, Ibid., 3, 4286 (1971).

[9] T. J. Wieting and J. L. Verble, in Electrons and Phonons in Layered Crystal Structures (T. J. Wieting and M. Schlüter, eds.), Reidel, Dordrecht, Holland, 1979, p. 321.

[10] A. W. Overhauser, Phys. Rev., 167, 691 (1968).

[11] E. A. Wood, Bell Syst. Tech. J., 43, 541 (1964).

[12] D. F. Hornig, J. Chem. Phys., 16, 1063 (1948).

[13] H. Winston and R. S. Halford, Ibid., 17, 607 (1949).

[14] S. Bhagavantam and T. Venkatarayudu, Theory of Groups and Its Applications to Physical Problems, Academic, New York, 1969.

[15] J. C. Decius and R. M. Hexter, Molecular Vibrations in Crystals, McGraw-Hill, New York, 1977.

[16] J. G. Hooley, in Preparation and Crystal Growth of Materials with Layered Structures (R. M. A. Lieth, ed.), Reidel, Dordrecht, Holland, 1977, p. 1.

[17] A. R. Verma and P. Krishna, Polymorphism and Plytypism in Crystals, Wiley, New York, 1966.

[18] J. Schoonman and R. M. A. Lieth, in Preparation and Crystal Growth of Materials with Layered Structures (R. M. A. Lieth, ed.), Reidel, Dordrecht, Holland, 1977, p. 35.

[19] C. Vettier and Y. B. Yelon, J. Phys. Chem. Solids, 36, 401 (1975).

[20] A. Narath and J. Schirber, J. Appl. Phys., 37, 1124 (1966).

[21] H. R. Oswald and R. Asper, in Preparation and Crystal Growth of Materials with Layered Structures (R. M. A. Lieth, ed.), Reidel, Dordrecht, Holland, 1977, p. 71.

[22] R. M. A. Lieth and J. C. J. M. Terhell, in Preparation and Crystal Growth of Materials with Layered Structures (R. M. A. Lieth, ed.), Reidel, Dordrecht, Holland, 1977, p. 141.

[23] J. A. Wilson, F. J. Disalvo, and S. Mahajan, Phys. Rev. Lett., 32, 882 (1974); Adv. Phys., 24, 117 (1975).

[24] R. M. A. Lieth, in Preparation and Crystal Growth of Materials with Layered Structures (R. M. A. Lieth, ed.), Reidel, Dordrecht, Holland, 1977, p. 225.

[25] N. Kuroda and Y. Nishina, Solid State Commun., 28, 439 (1978).

[26] N. Kuroda, Y. Nishina, H. Iwasaki, and Y. Watanabe, Ibid., 38, 139 (1981).

[27] J. H. C. Hogg and W. J. Duffin, Phys. Status Solidi, b18, 755 (1966).

[28] F. E. Faradev, N. M. Gasanly, B. N. Marvin, and N. N. Melnik, Ibid., b85, 381 (1978).

[29] P. Buck, in Preparation and Crystal Growth of Materials with Layered Structures (R. M. A. Lieth, ed.), Reidel, Dordrecht, Holland, 1977, p. 255.

[30] N. Morimoto, Mineral J. (Sapporo), 1, 160 (1954); see Fig. 1 of Ref. 7 for the structural arrangement of atoms.

[31] D. E. Moncton, J. D. Axe, and F. J. Disalvo, Phys. Rev. Lett., 34, 734 (1975).

[32] J. A. Holy, M. W. Klein, W. L. McMillan, and S. F. Meyer, Ibid., 37, 1145 (1976).

[33] D. E. Moncton, F. J. Disalvo, J. D. Axe, L. J. Sham, and B. R. Patton, Phys. Rev. B, 14, 3432 (1976).

[34] S. D. Ross, Inorganic Infrared and Raman Spectra, McGraw-Hill, London, 1972.

[35] C. Kittel, Introduction to Solid State Physics, 3rd ed., Wiley, New York, 1966.

[36] J. P. Mon, Compt. Rendus, 262B, 493 (1966).

[37] S. Nakashima, A. Yoshida, T. Fakumoto, and A. Mitsuishi, J. Phys. Soc. (Japan), 31, 1847 (1971).

[38] S. P. Srivastava and H. D. Bist, Phys. Status Solidi, b54, k9 (1972).

[39] G. Lucovsky and R. M. White, Nuovo Cimento, 38B, 290 (1977).

[40] Y. Marioka and I. Nakagawa, Spectroschim. Acta, 34A, 5 (1978).

[41] S. Nakashima, H. Katahama, M. Daimon, and A. Mitsuishi, Solid State Commun., 31, 913 (1979).

[42] S. Nakashima, M. Daimon, and A. Mitsuishi, J. Phys. Chem. Solids, 40, 39 (1979).

[43] C. Carabatos, C. R. Acad. Sci. Paris, Ser B, 272, 465 (1971).

[44] A. Grisel and Ph. Schmid, Phys. Status Solidi, b73, 587 (1976).

[45] S. Nakashima, Solid State Commun., 16, 1059 (1975).

[46] R. Zallen and M. L. Slade, Ibid., 17, 1561 (1975).

[47] W. M. Sears, M. L. Klein, and J. A. Morrison, Phys. Rev. B, 19, 2305 (1979).

[48] W. Bauhoffer, G. Guntherdot, E. Anastassakis, A. Frey, and G. Benedek, Ibid., 22, 5873 (1980).

[49] G. Benedek, I. Pollini, L. Piseri, and R. Tubino, Ibid., 20, 4303 (1979).

[50] G. Benedek and A. Frey, Ibid., 21, 2482 (1980). (The LO frequencies in Tables 11 and 12 are those calculated in this paper.)

[51] S. R. Kuindersma, Phys. Status Solidi, b107, K163 (1981).

[52] P. N. Ghosh, Solid State Commun., 16, 811 (1975).

[53] A. Anderson and J. P. Todoeschuck, Can. J. Spectrosc., 22, 113 (1977).

[54] M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford University Press, Oxford, 1954.

[55] T. Iri and G. Kuwabara, J. Phys. Soc. Jpn., 24, 127 (1968).

[56] T. E. Freeman and G. D. Jones, Phys. Rev., 182, 411 (1969).

[57] J. H. Cristie and D. J. Lockwood, Chem. Phys. Lett., 8, 120 (1971); D. J. Lockwood and J. H. Christie, Ibid., 9, 559 (1971).

[58] D. J. Lockwood, J. Opt. Soc. Am., 63, 374 (1973).

[59] J. A. Campbell, J. Phys. C, 11, L795 (1977).

[60] I. W. Johnstone, D. J. Lockwood, and G. Mischler, Ibid., 11, 2147 (1978).

[61] I. W. Johnstone, D. J. Lockwood, G. Mischler, J. R. Fletcher, and C. A. Bates, Ibid., 11, 4425 (1978).

[62] D. J. Lockwood, I. W. Johnstone, G. Mischler, and P. Carara, Solid State Commun., 25, 565 (1978).

[63] G. Mischler, M. C. Schmidt, D. J. Lockwood, and A. Zwick, Ibid., 27, 1141 (1978).

[64] D. J. Lockwood, D. Bertrand, P. Carara, G. Mischler, D. Brillerey, and C. Tenier, J. Phys. C, 12, 3615 (1979).

[65] N. Caswell and S. A. Solin, Solid State Commun., 27, 961 (1978).

[66] A. Rulmont, Spectrochim. Acta, 30A, 161 (1974).

[67] O. Oehler and Hs. H. Gunthard, J. Chem. Phys., 48, 2036 (1968).

[68] P. Dawson, C. D. Hadfield, and G. R. Wilkinson, J. Phys. Chem. Solids, 34, 1217 (1973).

[69] A. S. Davydov, Theory of Molecular Excitons, Plenum, New York, 1971.

[70] P. Dawson, J. Phys. Chem. Solids, 36, 1401 (1975).

[71] P. N. Ghosh, Solid State Commun., 19, 639 (1976).

[72] W. J. Stevens, G. Das, A. C. Wahl, M. Krauss, and D. Neumann, J. Chem. Phys., 61, 3686 (1974).

[73] P. N. Ghosh, in Recent Development in Condensed Matter Physics, Vol. 2 (J. T. Devreese, L. F. Lemmems, V. E. Van Doren, and J. Van Royen, eds.), Plenum, New York, 1981, p. 435.

[74] P. N. Ghosh, J. Phys. C, 9, 2673 (1976).

[75] D. R. Karecki and B. P. Clayman, Solid State Commun., 19, 479 (1976).

[76] D. R. Karecki and B. P. Clayman, Phys. Rev. B, 19, 6367 (1979).

[77] R. W. Ward, Infrared Phys., 16, 385 (1976).

[78] J. R. Duffey, R. D. Kirby, and R. V. Coleman, Solid State Commun., 20, 617 (1976).

[79] J. C. Tsang, J. E. Smith, Jr., M. W. Shafer, and S. F. Meyer, Phys. Rev. B, 16, 4239 (1977).

[80] J. E. Smith, Jr., J. C. Tsang, and M. W. Shafer, Solid State Commun., 19, 283 (1976).

[81] J. A. Holy, K. C. Woo, M. V. Klein, and F. C. Brown, Phys. Rev. B, 16, 3628 (1977).

[82] K. C. Woo and F. C. Brown, Solid State Commun., 28, 341 (1978).

[83] W. K. Unger, J. M. Reyes, O. Singh, A. F. Carzon, J. C. Irwin, and R. F. Frindt, Ibid., 28, 109 (1978).

[84] J. E. Smith, Jr., M. L. Nathan, M. W. Shafer, and J. B. Torrance, in Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Vol. II, Nauka, Leningrad, 1968, p. 1306.

[85] G. Lucovsky, R. M. White, J. A. Benda, and J. F. Revelli, Phys. Rev. B, 7, 3859 (1973).

[86] A. J. Smith, P. E. Meek, and W. Y. Liang, J. Phys. C, 10, 1321 (1977).

[87] J. L. Verble and T. J. Wieting, Phys. Rev. Lett., 25, 362 (1970).

[88] J. L. Verble, T. J. Wieting, and P. R. Reed, Solid State Commun., 11, 941 (1972).

[89] O. P. Agnihotri, H. K. Sehgal, and A. K. Garg, Ibid., 12, 135 (1973).

[90] J. M. Chen and C. S. Wang, Ibid., 14, 857 (1974).

[91] N. Wakabayashi, H. G. Smith, and R. M. Nicklow, Phys. Rev. B, 12, 659 (1975).

[92] R. Kaplan, Nuovo Cimento, 38B, 526 (1977).

[93] S. Uchida and S. Tanaka, J. Phys. Soc. Jpn., 45, 153 (1978).

[94] H. Rau, J. Phys. Chem. Solids, 41, 765 (1980).

[95] C. S. Wang and J. M. Chen, Solid State Commun., 14, 1145 (1974).

[96] D. G. Mead and J. C. Irwin, Can. J. Phys., 55, 379 (1977).

[97] P. C. Leung, G. Andermann, W. G. Spitzer, and C. A. Mead, J. Phys. Chem. Solids, 27, 849 (1966).

[98] G. B. Wright and A. Mooradian, Bull. Am. Phys. Soc., 11, 812 (1966).

[99] N. Kuroda, Y. Nishima, and T. Fukaroi, J. Phys. Soc. Jpn., 28, 981 (1970).

[100] T. J. Wieting and J. L. Verble, Phys. Rev. B, 5, 1473 (1972).

[101] M. Hayek, O. Brafman, and R. M. A. Lieth, Ibid., 8, 2772 (1973).

[102] J. L. Brebner, S. Jandl, and B. M. Powell, Solid State Commun., 13, 1555 (1973).

[103] J. C. Irwin, R. M. Hoff, B. P. Clayman, and R. A. Bromley, Ibid., 13, 1531 (1973).

[104] H. Yoshida, S. Nakashima, and A. Mitsuishi, Phys. Status Solidi, b59, 655 (1973).

[105] J. P. Van der Ziel, A. E. Meixner, and H. M. Kasper, Solid State Commun., 12, 1213 (1973).

[106] A. Mercier and J. P. Voitchovsky, Ibid., 14, 757 (1974).

[107] E. Finkman and A. Rizzo, Ibid., 15, 1841 (1974).

[108] R. M. Hoff, J. C. Irwin, and R. M. A. Lieth, Can. J. Phys., 53, 1606 (1975).

[109] S. Jandl, J. L. Brebner, and B. M. Powell, Phys. Rev. B, 13, 686 (1976).

[110] A. Polian, K. Kunc, and A. Kuhn, Solid State Commun., 19, 1709 (1976).

[111] V. Riede, H. Neumann, F. Levy, and H. Sobota, Phys. Status Solidi, b104, 277 (1981).

[112] V. Riede, H. Neumann, H. X. Nguyen, A. Sobota, and F. Levy, Physica, 100B, 355 (1980).

[113] N. Kuroda and Y. Nishina, Solid State Commun., 30, 95 (1979).

[114] N. Kuroda and Y. Nishina, Ibid., 34, 481 (1980).

[115] N. Kuroda, I. Munakata, and Y. Nishina, J. Phys. Soc. Jpn., to be published.

[116] N. Kuroda and Y. Nishina, J. Phys. (Paris), Colloq., to be published.

[117] R. M. Martin and J. C. Damen, Phys. Rev. Lett., 26, 86 (1971).

[118] H. Iwasaki, Y. Watanabe, N. Kuroda, and Y. Nishina, Physica, 105 B+C, 314 (1981).

[119] N. M. Gasanly, B. M. Yavadov, V. I. Tagirov, and E. A. Vinogradov, Phys. Status Solidi, b89, K43 (1978).

[120] F. E. Faradev, N. M. Gasanly, B. N. Mavrin, and N. N. Melnik, Ibid., b85, 38 (1978).

[121] N. M. Gasanly, N. F. Gakhramanov, B. M. Dzhavadov, V. I. Tagirov, and E. A. Vinogradov, Ibid., b95, K191 (1979).

[122] N. M. Gasanly, B. M. Dzhavadov, V. I. Tagirov, and E. A. Vinogradov, Ibid., b100, K53 (1980).

[123] F. Cerdeira, E. A. Menseses, and A. Gouskov, Phys. Rev. B, 16, 1648 (1977).

[124] J. C. Irwin, B. P. Clayman, and D. G. Mead, Ibid., 19, 2099 (1979).

[125] G. B. Abdullaev, L. K. Vodopyanov, K. R. Allakhverdiev, L. V. Golubev, S. S. Babarer, and E. Yu. Salaev, Solid State Commun., 31, 851 (1979).

[126] F. E. Faradzhev, N. M. Gasanly, A. S. Ragimov, A. F. Goncharov, and S. I. Subbolin, Ibid., 39, 587 (1981).

[127] C. Haas and M. M. G. Corbey, J. Phys. Chem. Solids, 20, 197 (1961).

[128] J. M. Chamberlain, S. S. Sirbegovic, and P. M. Nikolic, J. Phys. C, 7, L150 (1974).

[129] P. M. Nikolic, L. J. Miljkovic, P. Mihaljlovic, and B. Lavrencic, Ibid., 10, L289 (1977).

[130] H. R. Chandrasekhar, R. G. Humphreys, U. Zwick, and M. Cardona, Phys. Rev. B, 15, 2177 (1977).

[131] H. R. Chandrasekhar and U. Zwick, Solid State Commun., 18, 1509 (1976).

[132] D. I. Siapkas, D. S. Kyriakos, and N. A. Economou, Ibid., 19, 765 (1976).

[133] I. Gregora and N. Stetter, Phys. Status Solidi, b71, K187 (1975).

[134] J. D. Wiley, W. J. Buckel, and R. L. Schmidt, Phys. Rev. B, 13, 2489 (1976).

[135] H. R. Chandrasekhar, R. G. Humpherys, and M. Cardona, Ibid., 16, 2981 (1977).

[136] R. Zallen and M. L. Slade, Ibid., 9, 1627 (1974).

[137] R. Zallen, in Lattice Dynamics and Intermolecular Forces (S. Califano, ed.), Academic, New York, 1959, p. 159.

[138] R. Zallen, Phys. Rev. B, 9, 4485 (1971).

[139] D. Treacy and P. Taylor, Ibid., 11, 2941 (1975).

[140] A. P. DeFonzo and J. Tave, Ibid., 18, 6957 (1978).

[141] C. Razetti and P. P. Lottici, Solid State Commun., 29, 361 (1979).

[142] J. M. Besson, J. Carnagora, and R. Zallen, Phys. Rev. B, 22, 3866 (1980).

[143] N. M. Gasanly, B. N. Mavrin, Kh. E. Sterin, V. I. Tagirov, and Z. D. Khalafov, Phys. Status Solidi, b86, K49 (1978).

[144] N. A. Bakhyshov, N. M. Gasanly, B. M. Yavadov, V. I. Tagirov, and Sh. M. Efendiev, Ibid., b91, K1 (1979).

[145] N. M. Gasanly, B. M. Dzhavadov, V. I. Tagirov, and E. A. Vinogradov, Ibid., b95, K27 (1979).

[146] N. M. Gasanly, A. F. Goncharov, B. M. Dzhavadov, N. N. Melnik, V. I. Tagirov, and E. A. Vinogradov, Ibid., b92, K139 (1979).

[147] N. M. Gasanly, R. E. Guseinov, A. S. Ragimov, and V. I. Tagirov, Ibid., b101, K121 (1980).

[148] N. M. Gasanly, A. F. Goncharov, B. M. Dzhavadov, N. N. Melnick, V. I. Tagirov, and E. A. Vinogradov, Ibid., b97, 367 (1980).

[149] N. M. Gasanly, B. M. Dzhavadov, A. S. Ragimov, V. I. Tagirov, and R. E. Gaselnov, Physica, 112B, 78 (1982).
[150] T. J. Isaacs, J. Appl. Cryst., 6, 413 (1973).
[151] T. J. Isaacs and R. H. Hopkins, J. Cryst. Growth, 29, 121 (1975).
[152] T. J. Isaacs and J. D. Feicktner, J. Solid State Chem., 14, 260 (1975).
[153] H. Hahn and B. Wellmann, Naturwissenschaften, 54, 72 (1967).
[154] D. Muller, F. E. Poltmann, and H. Hahn, Z. Naturforsch., 29b, 117 (1974).
[155] D. Muller and H. Hahn, Z. Anorg. Allg. Chem., 438, 258 (1978).
[156] P. N. Ghosh, Phys. Rev. B, 18, 5615 (1978).
[157] T. J. Wieting, Solid State Commun., 12, 931 (1973).
[158] G. Lucazeau, Ibid., 18, 917 (1976).
[159] P. N. Ghosh and C. R. Maiti, J. Phys. C, 13, L37 (1980).
[160] C. R. Maiti and P. N. Ghosh, Solid State Commun., 42, 149 (1982).
[161] V. Y. Altshul, V. K. Bushenov, and J. Baumann, Exp. Tech. Phys., 29, 105 (1981).
[162] R. A. Bromley, Philos. Mag., 23, 1417 (1971).
[163] H. J. C. van der Valk and C. Haas, Phys. Status Solidi, b80, 321 (1977).
[164] C. R. Maiti and P. N. Ghosh, J. Phys. C, 11, 2475 (1978).
[165] P. N. Ghosh and C. R. Maiti, to be published.
[166] L. L. Boyer and J. R. Hardy, Phys. Rev. B, 7, 2886 (1973).
[167] P. N. Ghosh and C. R. Maiti, to be published.
[168] A. Pasternak, J. Phys. C, 9, 2987 (1976).
[169] A. Frey and R. Zeyher, Solid State Commun., 28, 435 (1978).
[170] G. C. Cran and M. J. C. Sangster, J. Phys. C, 7, 1937 (1974).
[171] W. B. Yelon, R. Scherm, and C. Vettier, Solid State Commun., 15, 391 (1974).
[172] S. Jandl and R. Provecher, J. Phys. C, 14, L461 (1981).
[173] B. T. Matthias, Phys. Rev. Lett., 27, 245 (1971).
[174] Y. Matthey, R. Clement, C. Sourisseau, and G. Lucazeau, Inorg. Chem., 19, 2773 (1980).