PHYSICAL REVIEW B VOLUME 18, NUMBER 10 15 NOVEMBER, 1978

Factor-group analysis of high-symmetry layer dynamics

Pradip N. Ghosh

Department of Physics, University of Calcutta 92, Acharya Prafulla Chandra Road, Calcutta-700009, India

(Received 14 December 1976; revised manuscript received 15 July 1977)

The method of factor-group analysis used for molecular crystals has been extended to the case of layer crystals which usually have very high symmetry. In case of such high-symmetry layer crystals, the optically active modes are divided into compressional and shear types. It is found that there is a one-to-one correspondence between a compressional and a doubly degenerate shear mode in case of the layer crystals in which each atomic sheet contains only one atom of the unit cell. Further it is shown that for such simple layer crystals the matrix for the transformation to symmetry coordinates is the same for both compression and shear motions. This leads to considerable simplification in the numerical solution of the dynamics of these structures. The numerical calculations for the intralayer modes of MoS_2, PbI_2, GaS, and GaSe are presented in both the nearest- and the second-nearest-neighbor approximations.

I. INTRODUCTION

A large number of inorganic molecular solids crystallize in layer structures. This group of crystals contains transition-metal chalcogenides, chalcogenides of gallium,[1] and a number of halide and hydroxide crystals.[2,3] The chalcogenide crystals exhibit a wide range of electrical properties: HfS_2 is an insulator, MoS_2, GaS, and GaSe are semiconductors, and NbS_2 and VSe_2 are metals, while $NbSe_2$ becomes a superconductor at a moderately high temperature. Recently, high-temperature superconductivity has been found by intercalating transition-metal dichalcogenides like MoS_2 with alkali and alkaline-earth metals.[4] Among the nonchalcogenide layer materials, the large family of layered halide[5] crystals forms structures of wide physical and chemical interest. It is interesting to note that these layer compounds, having a wide spectrum of physical and chemical properties, have very similar dynamical properties because of their similarity in crystal structure. Recently, a large number of Raman and infrared studies have been carried out on these layer compounds.[6-11] These studies can supplement further data on the results of x-ray and electron microscopic investigations[12] on such compounds. In fact, a knowledge of the dynamics of the unperturbed crystals is of great importance for an understanding of superconductivity of the intercalated compounds[4] as well as for the Jahn-Teller effect[5] and other optical experiments which are often carried out in layered host lattice structure. Our aim in this work is to perform a layer dynamics calculation for these crystals based on factor-group analysis with intralayer nearest- and second-nearest-neighbor force constants.

Layer crystals do not strictly conform to the usual definition of molecular crystals. Yet they are made up by stacking two-dimensional macroscopically extended gigantic molecular units[13] (the individual layers). As in the case of ordinary molecular solids the interlayer (or intermolecular) bonding is much weaker than the intralayer (or intramolecular) bonding. The layers have a diperiodic symmetry.[13,14] In the two directions parallel to the layers these crystals form network solids, while in the third direction perpendicular to the layer they form molecular solids. Each layer contains parallel sheets of atoms which are periodic in two dimensions and one can define a layer unit cell as containing one or more formula units. The crystal unit cell is composed of one or more layers depending on the space group. The difference in stacking sequence of the individual layers gives rise to different polytypes. Hence the layer symmetry should be distinguished from the crystal symmetry. The presence of more than one layer per crystal unit cell will give rise to Davydov splitting, similar to that in molecular crystals if the interlayer interaction is sufficiently strong. But in the case of a large number of crystals like MoS_2,[6] GaSe,[11] and PbI_2,[7] it has been found that the splitting is very small. This confirms the weakness of interlayer bonding. Thus, for all practical purposes, the vibrations of a layer crystal reduce to vibrations of each individual layer.

In each layer crystal in which each atomic sheet contributes only one atom to the crystal (or layer) unit cell one has an added advantage of dividing the intralayer modes into two types—compressional and shear. In case of compressional modes the atomic planes move rigidly against each other, while shear modes correspond to the rigid sliding of the planes over each other. But if the crystal unit cell contains more than one atom of each atomic sheet, then in addition to the rigid motion of the atomic planes there will be intraplane stretching and librational modes.[13] We shall be interested only with the former class of crystals and thus capitalize on the division into compressional and shear modes. It is interesting to note that this class of layer crystals has high symmetry (hexagonal and trigonal) and intralayer mode vibrational eigenvectors are directly determined by symmetry.[6] In fact, most familiar layer crystals usually have high symmetry.

We shall consider only the modes at the Brillouin-zone center ($q = 0$), so atoms in different layers move in phase. In Sec. II we introduce the method of obtaining the frequencies of symmetry modes starting from a potential function defined in terms of internal coordinates. In Sec. III we present the calculation for a few crystals with different factor-group symmetries and in Sec. IV discuss the results.

II. THEORY

Let $\underline{k}$ form an N-dimensional basis set containing unit vectors all oriented in directions perpendicular to the layers, where N is the number of atomic sheets per layer unit cell. The displacement for the compressional modes will be $\underline{k} \cdot \underline{z}$, where $\underline{z}$ is an N-dimensional column vector the elements of which are displacements perpendicular to the layers. Similarly if $\underline{i}$ forms a $2N$-dimensional basis set defined by unit vectors oriented in two mutually perpendicular directions along the plane of the layer, the shear displacement will be given by $\underline{i} \cdot \underline{w}$, $\underline{w}$ 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 $\underline{i}$. In case of mass-weighted Cartesian coordinates $\underline{Z}$ and $\underline{W}$, the displacement pattern will be $\underline{K} \cdot \underline{Z}$ and $\underline{I} \cdot \underline{W}$ for compressional and shear modes, respectively; $\underline{K}$ and $\underline{I}$ are the corresponding mass-weighted basis sets.

We start with a potential function defined in terms of internal coordinates r_i, chosen appropriately for the compressional and shear motion,

$$2V = \sum_{i,j} r_i f_{ij} r_j \,, \tag{1}$$

where f is the force-constant matrix, appropriate for compressional and shear modes. The transformation from Cartesian to internal coordinates is given by

$$r_i^c = P_{ij} z_j \tag{2}$$

in the case of compressional modes and a similar relation for shear coordinates in terms of w. We shall choose similar potential function models for both compression and shear motions. The potential function (1) may now be written in terms of mass-weighted Cartesian coordinates as

$$2V = \sum_{i,j} Z_i L_{ij} Z_j \,, \tag{3}$$

where

$$L_{ij} = \sum_{k,l} \frac{P_{ki} f_{kl} P_{lj}}{(m_i m_j)^{1/2}} \,. \tag{4}$$

A similar relation may also be written for shear modes. Using projection operator technique we can project out a symmetry adapted basis $\underline{\gamma}$ from the old basis vector $\underline{K}$, such that

$$\underline{\gamma} = \underline{K} \hat{R} \,. \tag{5}$$

Hence the displacement for compressions will be given by $\vec{\underline{\gamma}} \cdot \vec{\underline{S}}^c$ in terms of compressional symmetry coordinates

$$\underline{S}^c = \hat{R}^\dagger \underline{Z} \,. \tag{6}$$

Now the potential function (3) becomes

$$2V = \sum S_i F_{ij} S_j \,, \tag{7}$$

where,

$$F_{ij} = \sum_{k,l} R_{ki} L_{kl} R_{lj} \,. \tag{8}$$

In case of shear vibrations, the transformation to symmetry adapted basis vectors will combine only those vectors which are in one particular direction in the plane of the layer.[15] Hence the operations (5)–(7) may also be carried out for the shear modes and it is found that the force-constant matrix F is split up into two identical blocks, corresponding to the doubly degenerate shear modes.

III. RESULTS

In case of high-symmetry layer crystals with one atom contained in each atomic sheet, it is an interesting fact that to each compressional mode there corresponds a doubly degenerate shear mode. This follows from factor group analysis of layer-unit-cell modes. It is further convenient that the transformation matrix R defining symmetry adapted basis sets are identical for both compressional and shear modes. The immediate outcome of this fact is that the symmetrized force-constant matrix F, which will determine the eigenfrequencies for the symmetry modes are identical except for a difference in the numerical values of f for compression and shear, defining the starting potential [Eq. (1)]. Hence, diagonalization of one matrix will lead to frequencies for both the compressional and shear modes defined in terms of the respective force constants.

We shall present the results of calculation for a

TABLE I. Calculations for MoS_2 and PbI_2 in the nearest-neighbor approximation.

	MoS_2 Mode	MoS_2 Frequency (cm^{-1}) Theory	MoS_2 Frequency (cm^{-1}) Experiment[a]	Force constants (mdyn/Å) (Mo-S)	PbI_2 Mode	PbI_2 Frequency (cm^{-1}) Theory	PbI_2 Frequency (cm^{-1}) Experiment[b]	Force constants (mdyn/Å) (Pb-I)
Compression	A_1'	409[c]	409	3.16	A_{1g}	98[c]	98	0.72
	A_2''	528	470		A_{2u}	146	113	
Shear	E''	287[c]	287	1.55	E_g	79[c]	79	0.47
	E'	371	384		E_u	117	106	

[a] Reference 6. [b] Reference 8. [c] Matched.

number of layer crystals in which the layer unit cell belongs to the D_{3d} and D_{3h} factor groups. In each case we first choose a potential function in the nearest-neighbor approximation. The force constants for both the compressional and shear modes are obtained by matching the respective frequencies. These constants are then used to determine the remaining frequencies for the respective modes. The deviation of the calculated frequencies from the experimental values, in some cases, is due to the weakness of nearest-neighbor approximation. Hence, we introduce the second-nearest-neighbor interaction in the same model and the force constants are again calculated by matching the respective frequencies. We discuss the particular cases considered in the following.

A. MoS_2 and PbI_2

In molybdenite (MoS_2) crystal the metal atom is at the center of a prism and is coordinated with six sulphur atoms at the corners. Each layer is formed by alternately occupied prisms placed side by side. The layer symmetry is given by D_{3h} factor group. This gives $A_1'+A_2''$ compressional and $E'+E''$ shear intralayer optical modes. The different stacking sequences give rise to different polytypes. $2H$-MoS_2 has a two-layer crystal unit cell (D_{6h} factor group) with $A_{2u}+2B_{2g}+A_{1g}+B_{1u}$ compressional and $E_{1u}+2E_{2g}+E_{1g}+E_{2u}$ shear optical modes. These include both intra- and interlayer modes.

Layers of lead iodide crystal belong to the D_{3d} factor group. The metal atom is at the center of a puckered hexagon and is coordinates to six halogen atoms alternately placed at the corners of the hexagon. The optically active intralayer modes are $A_{1g}+A_{2u}$ for compression and E_g+E_u for shear. $2H$-PbI_2 has a one-layer unit cell, while $4H$-PbI_2 has a two-layer unit cell with C_{6v} factor group. The optically active modes for the latter polytype are $3A_1+2B_1$ for compression and $3E_2+2E_1$ for shear motion.

TABLE II. Force constants (mdyn/Å) for MoS_2 and PbI_2 in the second-nearest-neighbor approximation.[8]

	MoS_2 f(Mo-S)	MoS_2 f(S-S)	PbI_2 f(Pb-I)	PbI_2 f(I-I)
Compression	2.50	0.32	0.43	0.14
Shear	1.67	−0.05	0.37	0.04

We shall consider only intralayer modes given by the factor groups D_{3h} and D_{3d} for MoS_2 and PbI_2 respectively. It is found that the transformation matrix R for both of these is given by

$$\hat{R}=\begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{6} & 1/\sqrt{3} \\ 0 & -2/\sqrt{6} & 1/\sqrt{3} \\ -1/\sqrt{2} & 1/\sqrt{6} & 1/\sqrt{3} \end{bmatrix}. \qquad (9)$$

The results of calculation for these two crystals are given in Tables I and II.

B. GaS and GaSe

In these crystals two formula units form a layer. Two metal atoms are placed along the central axis of a prism, each of them being coordinated with the three chalcogen atoms at the corners of the prism and with the other metal atom. These prisms form a layer similar to MoS_2. The layer symmetry is given by a D_{3h} factor group and the optically active modes are $2A_1'+A_2''$ for compression and $2E''+E'$ for shear. Again the layer stacking gives rise to different polytypes of GaSe; namely, β, ϵ, and γ type. β-GaSe has a D_{6h} factor group with $2A_{1g}+A_{2u}+2B_{1u}+2B_{2g}$ compressional and $2E_{1g}+E_{1u}+2E_{2u}+2E_{2g}$ shear modes. In fact, splitting between Davydov multiplets which occurs due to the presence of more than one layer per crystal unit cell is very small, indicating weak interlayer coupling. Hence this will have very little effect on the intralayer vibrations. The transformation matrix R for intralayer modes of these crystals is given by

TABLE III. Calculations for GaSe and GaS in the nearest-neighbor approximation.

		GaSe				GaS			
		Frequency (cm^{-1})		Force constant (mdyn/Å)		Frequency (cm^{-1})		Force constant (mdyn/Å)	
	Mode	Theory	Experiment[a]	f(Ga–Se)	f(Ga–Ga)	Theory	Experiment[a]	f(Ga–S)	f(Ga–Ga)
Compression	A_1'	308[b]	308	1.21	1.11	361[b]	361	1.31	1.28
	A_1'	122	135			182	188		
	A_2''	236[b]	236			318[b]	318		
Shear	E''	250[b]	250	0.99	0.53	340[b]	340	1.12	1.23
	E''	94	60			174	74		
	E'	213[b]	213			294[b]	294		

[a] Reference 10.

[b] Matched.

$$\hat{R}=\frac{1}{2}\begin{bmatrix} 1 & 1 & 1 & 1 \\ -1 & 1 & -1 & 1 \\ 1 & -1 & -1 & 1 \\ -1 & -1 & 1 & 1 \end{bmatrix}. \qquad (10)$$

The results of the calculation for these crystals are given in Tables III and IV.

IV. DISCUSSION

It is found from Table I that the nearest-neighbor model gives results in good agreement with experimental findings for the shear modes in MoS_2.

The deviation is large for compressional modes in both MoS_2 and PbI_2 and also for shear mode in PbI_2. Accordingly, the second-nearest-neighbor force constants are large for these modes (Table II). It may be noted that in MoS_2 the second-nearest-neighbor force f' arises from S-S interaction, and the sulphur atoms are placed along the z axis. Hence sulphur-sulphur interaction is important only for motion along the z axis (compression). Hence the shear motion along x or y direction is very little affected by this interaction. In PbI_2, the second-nearest neighbor I-I interaction affects the compressional mode largely and the shear mode to some extent because the two iodine atoms are not placed along the z axis.

In GaSe and GaS (Table III), the results calculated in the nearest-neighbor approximation agree well with the experimental values for the compressional modes, but this is not so for the shear modes. This may be due to the fact that the second-nearest-neighbor Se(S)-Ga interaction is not along the z axis and it will have a large effect on the shear motion (Table IV).

Thus the results of calculation are consistent with the crystal structure data. Hence, for high-symmetry layer structures in which each atomic sheet contains only one atom of the unit cell, one can divide the modes into compressional and doubly degenerate shear modes and there is a one-to-one correspondence between the compressional and shear modes. We have shown that in such cases the projection operators for the two types of modes are the same which leads to considerable simplification in obtaining the eigenfrequencies. Hence one can very easily obtain an idea of the compressional and shear forces from the Raman and infrared data of these layer structures. These calculations may also be done for the polytypes having higher symmetries like D_{6h} or C_{6v}. In these cases one has to consider more than one layer in a unit cell. So the model needs to include the interlayer force constants also. But since the atomic sheets remain monatomic the procedure followed will remain the same and similar simplifications may be done. It may be noted that Wieting[16] used a linear-chain model with both in-

TABLE IV. Force constants (mdyn/Å) for GaSe and GaS in the second-nearest-neighbor approximation.

	GaSe			GaS		
	f(Se–Ga)	f(Ga–Ga)	f(Se–Ga)[a]	f(S–Ga)	f(Ga–Ga)	f(S–Ga)[a]
Compression	1.12	1.18	0.09	1.29	1.32	0.02
Shear	1.10	0.43	–0.09	1.32	0.71	–0.21

[a] Second-nearest-neighbor force.

terlayer and intralayer force constants in the nearest-neighbor approximation for MoS_2 and GaSe crystals. It was found that the interlayer forces are 100 times smaller than the intralayer ones. Our calculations indicate that the second-nearest-neighbor forces are more important than the interlayer forces. The method presented in this paper is not applicable to crystals like arsenic chalcogenides[13] in which atomic sheets are not monatomic and also to the less familiar low-symmetry layer crystals.

ACKNOWLEDGMENT

The author thanks Professor D. L. Bhattacharya for many helpful discussions.

---

[1] J. A. Wilson and A. D. Yoffe, Adv. Phys. 18, 193 (1969).

[2] N. Wakabayashi, H. G. Smith, and R. Shanks, Phys. Lett. 50A, 367 (1974).

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

[4] B. T. Matthias, Phys. Rev. Lett. 27, 245 (1971).

[5] T. E. Freeman and G. D. Jones, Phys. Rev. 182, 411 (1969); D. J. Lockwood and J. H. Christie, Chem. Phys. Lett. 9, 559 (1971).

[6] T. J. Wieting and J. L. Verble, Phys. Rev. B 3, 4286 (1971).

[7] R. Zallen and M. L. Slade, Solid State Commun. 17, 1561 (1975).

[8] A. Grisel and Ph. Schmid, Phys. Status Solidi B 73, 587 (1976).

[9] G. Lucovsky, R. M. White, W. Y. Liang, R. Zallen, and Ph. Schmid, Solid State Commun. 18, 811 (1976).

[10] E. Finkman and A. Rizzo, Solid State Commun. 15, 1841 (1974).

[11] M. Hayek, O. Brafman, and R. M. A. Lieth, Phys. Rev. B 8, 2772 (1973).

[12] J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. 24, 117 (1975).

[13] R. Zallen, in *Lattice Dynamics and Intermolecular Forces*, edited by S. Califano (Academic, New York, 1975), p. 159; R. Zallen, M. L. Slade, and A. T. Ward, Phys. Rev. B 3, 4257 (1971).

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

[15] D. J. Lockwood, J. Opt. Soc. Amer. 63, 374 (1973).

[16] T. J. Wieting, Solid State Commun. 12, 931 (1973).