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Interlayer potential in $2H$-MoS$_2$

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An (exp-6)—type interlayer potential function is computed from factor-group analysis of intralayer and interlayer vibration frequencies in layered $2H$-MoS$_2$ crystal. Such a potential function allows one to include distant-neighbor interactions. For nonbonded intralayer interactions, only Coulombic interactions are considered. In the case of electrically neutral layers, interlayer ionic interactions are not important. This also allows us to confine the lattice sums to two dimensions. The equilibrium conditions, based on invariance of the lattice under internal and external strain, are used to eliminate a few parameters in the potential function. An iterative least-squares-fit method is presented for deriving the potential parameters from the observed vibrational frequencies.

I. INTRODUCTION

Vibrational spectra of layer crystals attracted attention of spectroscopists over the last few years. A large number of Raman and infrared spectroscopic investigations have been reported in the literature.[1] The major aim of these works is to analyze the effect of two-dimensional nature of the crystals on their dynamical properties. The presence of a weak interlayer interaction gives rise to small Davydov-type splitting[2,3] and low-frequency rigid-layer modes[4] observed in the far-infrared region. As an attempt to understand the observed spectra and also to translate these data into information about the bonding nature in these crystals, particularly the ratio of intralayer-interlayer forces,[5] a number of theoretical model calculations[6–12] were reported in the past for calculations of optical modes. The chief motivation of these works was to reproduce the observed data at the Brillouin-zone center by fitting a set of force-constant parameters. These studies are broadly of two types—the linear-chain model and the atom-atom—force model. The linear-chain model formulated by Wieting[6] for MoS$_2$ and GaSe and also by Ghosh[7] for the CdCl$_2$-type crystals, along with the modification by Ghosh and Maiti,[11] is based on the factor-group analysis of the normal vibrations[13] in terms of compressional and shear forces between different sheets of atoms (sublayers) that constitute a complete layer. On the other hand, the atom-atom—force model by Maiti and Ghosh[8] carries out the factor-group analysis of the normal modes in terms of the atom-atom—bond forces. These studies generate information about atomic binding which is of more immediate interest to chemists. Recently, Altshul *et al.*[10] have pointed out that the linear-chain model is not rotationally invariant, whereas the atom-atom model is, although the latter model calculates the rigid-layer frequency at a much lower value. The major deficiency of all these models is in the process of fitting the limited amount of observed data to reproduce a few force-field parameters. Thus the model calculations have to be limited to the nearest- and next-nearest-neighbor interactions and the more-distant-neighbor forces have to be left out of the model, although that is not always justified. This is the main reason for the deviation of the calculated data from the observed ones. As an attempt to overcome this problem partially, we present a calculation based on an empirical potential function for interlayer and nonbonded intralayer interactions. The potential functions expressed in terms of a few adjustable parameters can be used to extend the lattice sums up to any desired distance, in principle, from the reference atom.

Calculations have been carried out for $2H$-MoS$_2$ containing two layers in a primitive unit cell. Both the linear-chain model and the atom-atom—force model have been applied to this crystal previously.[3,6,8] However, the interlayer S-S potential function was always confined to the nearest neighbors. The role of more distant neighbors has never been carefully studied.

II. THEORY

In the case of layered crystals, the weak interlayer force is of van der Waals type, so that each layer is electrically neutral. The lattice attains stability when the weak force across the interlayer gap is balanced by the intralayer forces on the atoms in the surface of the layer. In the case of MoS$_2$, the sulfur atoms on the surface layer are bonded covalently to the molybdenum atoms sandwiched between the sulfur planes. In addition to this strong bonding, the sulfur atoms have both a strong Coulombic and weak van der Waals—type interaction with distant-neighbor atoms within the layer. The Coulombic interaction is of long-range type and dominates over the short-range van der Waals forces. Hence we shall restrict ourselves only to the Coulombic interaction for nonbonded intralayer interactions. The van der Waals—type interlayer interaction between the sulfur planes is assumed to be a pairwise potential of exp-6 type,

$$V(r_{ij})=A_{ij}\exp(-b_{ij}r_{ij})-C_{ij}/r_{ij}^6\ , \tag{1}$$

where A_{ij}, b_{ij}, and C_{ij} are the Williams parameters for the pair (i,j). The potential energy for the bonded atoms (Mo—S) within a layer is given as

$$V_{\text{intra}}=\tfrac{1}{2}K(\delta r)^2\ , \tag{2}$$

where $K=(\partial^2V/\partial r^2)_{r=r_0}$; the interatomic separation is assumed to be such that each atom is in a position of minimum potential energy. The electrostatic force within the layer for nonbonded atoms is

$$V_{\text{intra}}(r_{ij})=e_i e_j / r_{ij} \ . \tag{3}$$

In the case of intralayer bonded atoms only Mo—S bond-stretching force constants are included. The bond-bending forces may be important. However, this would involve next-nearest-neighbor (i.e., intralayer S-S) interactions. Such forces are implicitly taken into account by the inclusion of the Coulombic potential function [Eq. (3)] for all the nonbonded atoms within the layer. This enables us to circumvent the problem of introducing another force constant such as the S $\cdots$ S bond-stretching constant normally used in the central force-field model or the bond-bending forces used in the valence force-field model. In fact, in calculations involving such a force constant this constant alone has to account for all the distant-neighbor interactions.

With this definition of the potential functions we can calculate the elements of the force-constant matrix[8]

$$K_{\alpha\beta}(\kappa,\kappa')=(m_\kappa m_{\kappa'})^{-1/2}\sum_{l'}\frac{\partial^2 V}{\partial u_\alpha(l,\kappa)\partial u_\beta(l',\kappa')} \ , \tag{4}$$

which defines the force experienced by the κth atom in the direction α in a given layer l due to the displacement in the direction β of the κ'th atom in all the layers. Such a force-constant matrix can be block-diagonalized by means of a similarity transformation with the projection operator as discussed earlier.[3,13]

The solution of the secular determinant is subject to constraints imposed by the equilibrium condition of the lattice. This arises because of using analytic forms for the nonbonded potential such that $\partial V/\partial r_{ij}\neq 0$. The equilibrium of the lattice demands that the total potential energy be invariant with respect to rigid translation and rotation.[14] These conditions were first formulated by Boyer and Hardy.[15] If the displacement $u_\alpha(l,\kappa)$ is given by

$$u_\alpha(l,\kappa)=u_\alpha(\kappa)+\sum_\beta R_{\alpha\beta}\chi^0_\beta(l,\kappa) \ , \tag{5}$$

then

$$\frac{\partial V}{\partial u_\alpha(\kappa)}=0 \ \text{ for all } \alpha \text{ and } \kappa \ , \tag{6}$$

$$\frac{\partial V}{\partial R_{\alpha\beta}}=0 \ \text{ for all } \alpha\beta \ , \tag{7}$$

where $u_\alpha(\kappa)$ is the displacement of the κth atom in the α direction in the unit cell and produces internal strain, $\chi^0_\beta(l,\kappa)$ is the equilibrium position of the (l,κ)th atom, and $R_{\alpha\beta}$ is the external strain which produces a net rotation of the complete unit cell. The first of these equations states that the net force on any sublattice in the crystal is zero, while the second equation states that the total macroscopic stress is zero.

III. CALCULATIONS

The primitive unit cell of 2H-MoS$_2$ contains two layers (Fig. 1) and the crystal factor group is D_{6h}. The factor-group analysis leads to the symmetry modes $(A_{1g}+2A_{2u}+2B_{2g}+B_{1u}+E_{1g}+2E_{1u}+2E_{2g}+E_{2u})$. The symmetry coordinates for the nondegenerate modes corresponding to the displacements of the atoms along the Z axis (perpendicular to the layers) are given in Table I. The symmetry coordinates for the degenerate E modes may be expressed in the same way in terms of displacements along x or y directions parallel to the layers.

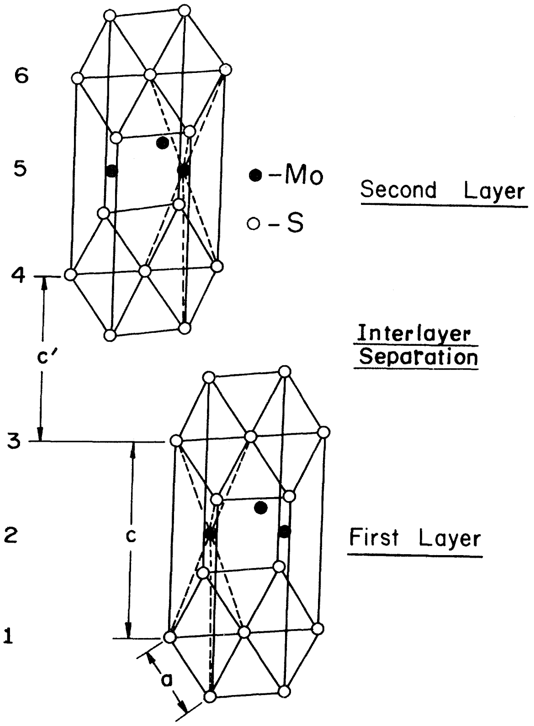

FIG. 1. Layered structure of 2H-MoS$_2$. Only one hexagon of each layer is shown. The complete layer is formed by repetition of these hexagons side by side (a=3.16, c=3.185, and c'=2.96 Å).

The evaluation of force-constant matrix elements depends on the choice of potential function parameters. We assume that the residual electric charge on Mo is twice that in S, i.e., $e_{\text{Mo}}=-2e_{\text{S}}$. Since the interlayer potential is only between sulfur atoms we use three parameters, A, b, and C, for this pair in the potential [Eq. (1)]. Hence the total number of potential function parameters is five—K, e_{S}, A, b, and C. For the calculation of lattice sums in the force-constant matrix we extend the range up to 5 Å from the reference atom. The more-distant-neighbor effects are

TABLE I. Symmetry coordinates of 2H-MoS$_2$.

Mode	Symmetry coordinates
S$_1$ (A_{1g})	$\frac{1}{2}(z_1-z_3+z_4-z_6)$
S$_2$ (B_{2u})	$\frac{1}{2}(-z_1+z_3+z_4-z_6)$
S$_3$ (A_{2u})	$1/\sqrt{6}(z_1+z_2+z_3+z_4+z_5+z_6)$
S$_4$ (A_{2u})	$1/\sqrt{12}(z_1-2z_2+z_3+z_4-2z_5+z_6)$
S$_5$ (B_{2g})	$1/\sqrt{12}(z_1-2z_2+z_3-z_4+2z_5-z_6)$
S$_6$ (B_{2g})	$1/\sqrt{6}(z_1+z_2+z_3-z_4-z_5-z_6)$

omitted from these calculations; the justification for this assumption will be given later. The solution of the secular determinant obtained with the help of the symmetry-transformation matrix gives the following expressions for the ten optically active frequencies:

$$\begin{aligned}
&\omega_1^2(A_{1g})=3[K\xi+e_s^2(\eta+\psi)+2f_1(A,b,C)]/m\ ,\\
&\omega_2^2(B_{1u})=3[K\xi+e_s^2(\eta+\psi)]/m\ ,\\
&\omega_3^2(A_{2u}^1)=0\ ,\\
&\omega_4^2(A_{2u}^2)=6(K\xi+e_s^2\eta)/\mu\ ,\\
&\omega_{5,6}^2(B_{2g}^{1,2})=\lambda_1\pm[\lambda_1^2-36(K\xi+e_s^2\eta)f_1(A,b,C)/mM]^{1/2}\ ,\\
&\omega_7^2(E_{1g})=3[K(1-\xi)+e_s^2(\eta'+\psi')+2f_2(A,b,C)]/2m\ ,\\
&\omega_8^2(E_{2u})=3[K(1-\xi)+e_s^2(\eta'+\psi')]/2m\ ,\\
&\omega_9^2(E_{1u}^1)=0\ ,\\
&\omega_{10}^2(E_{1u}^2)=3[K(1-\xi)+e_s^2\eta']/\mu\ ,\\
&\omega_{11,12}^2(E_{2g}^{1,2})=\lambda_2\pm\{\lambda_2^2-9[K(1-\xi)+e_s^2\eta']\\
&\qquad\qquad\times f_2(A,b,C)/mM\}^{1/2}\ ,
\end{aligned}\tag{8}$$

where

$$f_1(A,b,C)=Ab\sum_{i=1,2}(b\phi_i-\gamma_i)\exp(-br_i)+6C\tau\ ,$$

$$f_2(A,b,C)=Ab\sum_{i=1,2}(b\phi_i'-\gamma_i')\exp(-br_i)+6C\tau'\ ,$$

$$\lambda_1=\omega_4^2/2+3f_1(A,b,C)/m\ ,$$

$$\lambda_2=\omega_{10}^2/2+3f_2(A,b,C)/2m\ ,$$

$$\mu=2mM/(M+2m),$$

m is equal to the mass of S atom, M is equal to the mass of Mo atom, and ξ, η, etc., are constants depending on geometric parameters. The values of these constants are listed in Table II. Thus the frequency expressions are nonlinear functions of crystal structure and potential function parameters.

TABLE II. Geometrical parameters (in cgs units) used in frequency calculations.

Parameter	Value
ξ	0.4324
η	3799
ψ	14 731
η'	−436
ψ'	−5062
ϕ_1	503
γ_1	55
ϕ_2	276
γ_2	89
ϕ_1'	191
γ_1'	344
ϕ_2'	419
γ_2'	206
τ	−0.974
τ'	−4.26
r_1 (Å)	3.477
r_2 (Å)	4.698

The equilibrium condition [Eq. (6)] with respect to the internal strain gives only one equation for the sulfur atom along the Z axis. The sulfur atom is symmetrically surrounded in the plane of the layer, and thus the X or Y component of the force acting on this atom is identically zero. Since the Mo atom is surrounded symmetrically, the net force acting on it vanishes identically. The rotational-invariance condition [Eq. (7)] is tensorial in nature, and we have only two components, XX and ZZ. Thus we obtain three additional nonlinear equations among the unknown parameters.

In our case we have seven observed frequencies, which together with the three equations arising from the equilibrium of the lattice, can determine the five parameters. However, since the equations are nonlinear, we have to follow an iterative least-squares-fit method. The method consists of the following steps.

(1) Choose a set of guess values x_j^0 for the unknown parameters x_j. Calculate the difference between the observed value y_i and the value y_i^0 calculated with the guess values.

(2) With the use of analytic forms of the derivatives $g_{ij}=\partial y_i/\partial x_j$, calculate their initial values with the guess value x_j^0.

(3) Set up the normal equations

$$\vec{\mathrm{Y}}=\underline{G}\vec{\mathrm{X}}\ ,$$

where $\vec{\mathrm{Y}}$ is the column vector with the elements Y_j defined for M unknown parameters. We have

$$Y_j=\sum_{i=1}^{N}W_ig_{ji}dy_i,\quad j=1,2,\ldots,M\ ,$$

where W_i is the weight factor given to the ith observed data, $\vec{\mathrm{X}}$ is a column vector with M elements dx_j, and G is the $M\times M$ matrix defined by

$$G_{jk}=\sum_{i=1}^{N}W_ig_{ji}g_{ki}\ .$$

TABLE III. Calculation of frequencies (in cm^{-1}) in $2H$-MoS_2.

Mode	Observed[a]	Calculated
A_{1g}	409	384
B_{1u}		368
A_{2u}^1	0	0
A_{2u}^2	470	476
B_{2g}^1		483
B_{2g}^2	56	68
E_{1g}	287	301
E_{2u}		298
E_{1u}^1	0	0
E_{1u}^2	384	385
E_{2g}^1	383	387
E_{2g}^2	34	28

[a] References 9 and 16.

TABLE IV. Calculation of potential function parameters.

Parameter	This work	Rinaldi and Pawley[a]	Kurittu[b]
K (m dyn/Å)	1.966		
e_s (electronic charge)	−0.315		
A (K cal/mol)	848 163	533 829	106 190
b (Å^{-1})	3.938	4.0	3.2
C (K cal/mol Å^6)	3583	1005	2571

[a]Reference 16.
[b]Reference 17.

(4) Solve these equations for dx_j with the known initial values for Y_j and G_{jk} defined for the guess values x_j^0. Add these dx_j to x_j^0, so that $x_j^1 = x_j^0 + dx_j$.

(5) Repeat the process with the new values x_j^1 until convergence is obtained.

In our case three of the five unknown parameters could be eliminated by using the three equations arising from the equilibrium conditions. Thus we are left with two unknown constants K and A, while the number of observed data available from Raman and ir measurements is seven. We used $W_i = 1$ for all the observed frequencies. The least-squares-fit program converged after four iterations. This process determines the two constants K and A, which yield the other constants b, C, and e_s^2. The values of the observed and calculated frequencies are presented in Table III, while the fitted parameters are given in Table IV.

IV. DISCUSSIONS

In this work we have presented a method of calculation of the vibrational spectrum of a layered-crystal $2H$-MoS_2 using an analytic form for the interlayer potential and a Coulombic potential for the nonbonded intralayer interactions. It may be noted that the lattice sum for the Coulombic interactions is not convergent for a three-dimensional lattice and one should employ the Ewald summation technique for this purpose. In our case, we have to carry out a two-dimensional lattice sum since each layer is electrically neutral. In this case as well, the Coulombic interaction is slowly convergent. However, the small contribution from the Coulombic interaction as evidenced by the small value of e_s^2 obtained by us shows that direct lattice summation is sufficient. This is also corroborated by the fact that MoS_2 is not known to be ionic. It has been verified that the inclusion of more-distant-neighbor interactions do not modify the results. This method is, however, approximate, and for a truly ionic crystal a proper lattice-summation method should be considered.

We have considered only Coulombic interactions for the nonbonded pairs, and the van der Waals interactions are neglected because they are small and fall off rapidly with distance. In fact, an Mo-S nonbonded exp-6 potential function can be incorporated in this model. But this would involve three more unknown parameters. In view of the limited number of observed data, it has not been attempted in this work.

The potential function parameters A, b, and C in the S ⋯ S pair for the lattice states of orthorhombic sulfur were calculated by Rinaldi and Pawley.[16] They calculated a series of values of the three potential function parameters by varying the value of b from 2.8 to 4.0 Å^{-1}, and proposed that a comparison of the calculated frequencies with the assigned spectroscopic data would lead to a choice of the b value and hence the other two parameters. In our work the values of A, b, and C are obtained by least-squares fit of the calculated frequencies with the observed data, and the fitted value of b is close to the 4.0-Å^{-1} value of Rinaldi and Pawley.[16] Hence we have presented all three of their parameters in Table IV for comparison with our data. It may be noted that the agreement is fair. More recently, Kurittu[17] has presented a detailed calculation of these parameters for S ⋯ S bonding. He obtained $b = 3.2$ Å^{-1} (these values are also included in Table IV for comparison).

The calculated values of frequencies are in fair agreement with the observed ones. The notable discrepancy is that the observed Davydov splitting could not be reproduced, and, as previously obtained by us[3] and other workers,[18,19] we obtain $E_{2g}^1 > E_{1u}^2$, a contradiction of the observed finding. This discrepancy was discussed by us in a previous paper,[3] and we believe that in calculations of Davydov splitting, higher-order multipole interaction should be taken into account.

In spite of the limitations in the proposed model we have successfully developed a potential function for the interlayer gap. Such a model can be easily extended to other high-symmetry layered crystals for obtaining the interlayer potential function.

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[1] P. N. Ghosh, in *Applied Spectroscopy Reviews,* edited by E. G. Brame, Jr. (Dekker, New York, 1983), Vol. 19(2), pp. 259–323.

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

[3] P. N. Ghosh and C. R. Maiti, Phys. Rev. B 28, 2237 (1983).

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

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

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

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

[8] C. R. Maiti and P. N. Ghosh, J. Phys. C 11, 2475 (1978).

[9] A. Pasternak, J. Phys. C 9, 2987 (1976).

[10] V. Ya. Altshul, V. K. Bashenov, and J. Baumann, Exp. Tech.

Phys. 29, 105 (1981).

[11] P. N. Ghosh and C. R. Maiti, J. Phys. C 13, L37 (1980).

[12] C. R. Maiti and P. N. Ghosh, Solid State Commun. 42, 149 (1982).

[13] P. N. Ghosh, Phys. Rev. B 18, 5615 (1978).

[14] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1964).

[15] L. L. Boyer and J. R. Hardy, Phys. Rev. B 7, 2886 (1973).

[16] R. P. Rinaldi and G. S. Pawley, Il Nuovo Cimento 16B, 55 (1973).

[17] J. V. E. Kurittu, Phys. Scr. 21, 194 (1980); 21, 200 (1980).

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

[19] N. Kuroda and Y. Nishina, Phys. Rev. B 19, 1312 (1979).