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Interlayer force and Davydov splitting in $2H$-MoS$_2$

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The atom-atom interaction model has been extended to the case of $2H$-MoS$_2$ and it is shown that the observed vibrational frequencies can be satisfactorily reproduced by only three force constants. However, the calculation leads to a frequency reversal in the Davydov pair which is very similar to that found earlier for ϵ-GaSe and β-GaS. Since MoS$_2$ is somewhat less ionic than the two gallium compounds, we suggest that the frequency reversal may not be due to the long-range interactions proposed earlier. We discuss the possible role of short-range multipolar interactions.

The layer dynamics of MoS$_2$ has been of considerable interest in recent years. The theoretical analysis of observed optical vibration frequencies was first carried out by Bromley.[1] He used a central-force model to obtain the ratio of Mo-S and S-S force constants. The interlayer forces were not taken into account in his model. Verble *et al.*[2] proposed a rigid-layer model based on central forces to obtain the ratio of nearest-neighbor interlayer force constants K^c and K^s, parallel and perpendicular to the c axis, respectively, in terms of the angle θ between the S-S interlayer bond and the basal plane, as $K^c/K^s = \frac{3}{2}\tan\theta$. In the case of $2H$-MoS$_2$, with $\theta = 60.1°$, this gives $K^c/K^s = 2.61$. Wieting[3] proposed a linear-chain model which leads to a value of 2.86 for the same ratio[4] based on the observed data. Webb *et al.*[5] later showed that the expression for K^c/K^s derived by Verble *et al.*[2] should be corrected to $K^c/K^s = 2\tan^2\theta$, hence the value of K^c/K^s would be 6.0, which is in serious disagreement with the observation. This shows the inadequacy of the central-force model based on rigid-layer dynamics. Wakabayashi and Nicklow[6] used axially symmetric and valence-force-field models for the lattice-dynamical analysis over the complete Brillouin zone. We[7] recently proposed a simple atom-atom interaction model to calculate the optical vibration frequencies of a single layer of MoS$_2$ in terms of the atom-atom force constant and crystal structure parameters. The model can provide direct information of bond forces. Altshul *et al.*[8] used this atom-atom interaction model for ϵ-GaSe having two layers in a crystal unit cell and obtained good agreement with experimental values. In this Brief Report we show how the atom-atom interaction model can be extended to $2H$-MoS$_2$ with two layers in a crystal unit cell, and all the optical vibration frequencies can be calculated by adjusting only three parameters representing the atom-atom bond forces. This model allows us to express both the interlayer frequencies in terms of only one interlayer force constant in addition to the intralayer ones, thus circumventing the problem of defining the ratio of the two interlayer force constants as defined in the rigid-layer model.[2]

The primitive unit cell of $2H$-MoS$_2$ contains two layers and the crystal factor group is D_{6h}. The layers are identical in the sense that each layer contains three sublayers, one sublayer of Mo atoms being sandwiched between the two planes of sulfur atoms. One layer of the crystal unit cell is rotated and translated with respect to the other layer in such a way that a line drawn parallel to the c axis and passing through the Mo atom in the first layer will pass through the two S atoms of the second layer (Fig. 1). The atomic distances are $a = 3.16$ Å, $c = 3.185$ Å, and $c' = 2.96$ Å.

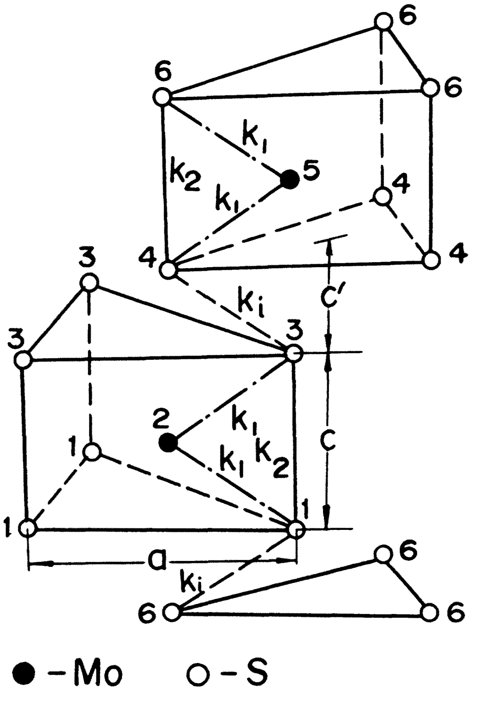

FIG. 1. Intra- and interlayer force constants in $2H$-MoS$_2$.

The factor group analysis of the normal vibrations leads to the modes

$$2A_{2u}+A_{1g}+2B_{2g}+B_{1u}+2E_{2g}+E_{2u}+2E_{1u}+E_{1g}\ .$$

In the atom-atom interaction force model[7] we introduce the two intralayer force constants K_1 and K_2 and the interlayer force constant K_i (Fig. 1). Following the procedure presented in Ref. 7, we obtain the following expressions for optical vibration frequencies:

$$\omega_1^2(A_{1g})=\frac{3}{m}(K_1\xi+2K_2/3+2K_i\eta)\ ,$$

$$\omega_2^2(B_{1u})=(3/m)(K_1\xi+2K_2/3)\ ,$$

$$\omega_3^2(A_{2u}^1)=0\ ,$$

$$\omega_4^2(A_{2u}^2)=(6/\mu)K_1\xi\ ,$$

$$\begin{aligned}\omega_{5,6}^2(B_{2g}^{1,2})=\omega_4^2/2+(3/m)K_i\eta\\ \pm\{[\omega_4^2/2+(3/m)K_i\eta]^2\\ -36K_1K_i\xi\eta/mM\}^{1/2}\ ,\end{aligned}$$

$$\omega_7^2(E_{1g})=(3/2m)K_1\xi'+(3/m)K_i\eta'\ ,$$

$$\omega_8^2(E_{2u})=(3/2m)K_1\xi'\ ,$$

$$\omega_9^2(E_{1u}^1)=0\ ,$$

$$\omega_{10}^2(E_{1u}^2)=(3/\mu)K_1\xi'\ ,$$

$$\begin{aligned}\omega_{11,12}^2(E_{2g}^{1,2})=\omega_{10}^2/2+(3/2m)K_i\eta'\\ \pm\{[\omega_{10}^2/2+(3/2m)K_i\eta']^2\\ -9K_1K_i\xi'\eta'/mM\}^{1/2}\ ,\end{aligned}$$

where $\xi=3c^2/(3c^2+4a^2)$, $\xi'=1-\xi$, $\eta=3c'^2/(3c'^2+a^2)$, $\eta'=1-\eta$, and $\mu=mM/(m+M)$, with m being the mass of sulfur atom and M the mass of molybdenum atom. Thus all the frequencies are expressed in terms of three force constants and the crystal structure parameters. From the infrared and Raman studies of Wieting and Verble[9] and the neutron scattering studies of Wakabayashi *et al.*,[6] we have seven observed frequencies. These are used to obtain the three force constants. The calculated and observed values are listed in Table I together with the derived force constants. The agreement of the calculated and observed frequencies is good. The small value of the interlayer force constant proves the weakness of the interlayer bonding with respect to the intralayer ones. The major discrepancy in the calculation is the reversal of sign of the Davydov splitting, which is calculated as -2 cm^{-1} compared to the experimental value of $+1$ cm^{-1}. This is also related to the large difference between the calculated and observed values of the interlayer E_{2g}^2 mode (Table I). A similar reversal in the sign of the Davydov splitting was observed by Wieting and Verble[10] for ϵ-GaSe. They found that the frequency difference of the Davydov doublet $E_{1u}-E_{2g}$ is contrary to what is calculated from the van der Waals interaction. They concluded that this reversal might be caused by the long-range Coulomb interaction. In the case of β-GaS, Kuroda and Nishina[11] observed a similar frequency reversal and showed that this anomaly cannot be explained in terms of the long-range Coulomb interaction in the deformation-dipole approximation. The frequency reversal obtained in our atom-atom interaction calculation for $2H$-MoS$_2$ leads to the fact that this phenomenon is common to all the three crystals—$2H$-MoS$_2$, ϵ-GaSe, and β-GaS. Hence it may not be due to the long-range interactions because MoS$_2$ is known to be less ionic than the other two compounds.

TABLE I. Calculation of frequencies and force constants in $2H$-MoS$_2$.

Modes	Frequencies (cm^{-1})		Force constants (mdyne Å^{-1})
	Obs.[a]	Calc.	
A_{1g}	409	409	
B_{1u}		399	
A_{2u}^1	0	0	
A_{2u}^2	470	470	
B_{2g}^1		479	$K_1=1.92$
B_{2g}^2	56	56.7	$K_2=0.36$
E_{1g}	287	296.6	$K_i=0.037$
E_{2u}		294	
E_{1u}^1	0	0	
E_{1u}^2	384	381	
E_{2g}^1	383	383	
E_{2g}^2	33.7	25	

[a] Reference 9 and Ref. 6.

The magnitude and sign of the Davydov splitting depends on the interaction of all the multipole moments which change during the vibration. In the case of Davydov splitting of the OH stretching frequency in Ca(OH)$_2$ and Mg(OH)$_2$ crystals it was found that the dipole-dipole interaction leads to a sign of the splitting which is contrary to the experimental value.[12] However, the sign anomaly could be solved after introducing the quadrupole-quadrupole interaction. A similar preponderant role of the quadrupolar interactions in the Davydov splitting were found in cases of a few other inorganic crystals containing small molecules.[13] Thus the splitting originates not only from the interaction of transition moments but also from the short-range multipolar interactions which are present in the system even before the vibrational excitation. These short-range interactions are not explicitly taken into account in our atom-atom empirical force constants or in the calculations based on the van der Waals interaction and could be responsible for the observed anomalous Davydov splitting in layer crystals. However, in such cases the observed data are rather scanty and the quadrupole moment derivatives for the corresponding normal modes are not available, thus making any such calculation not feasible at the moment. It may be mentioned that more detailed and reliable measurements of Davydov splittings in the low-symmetry layer crystals As_2S_2 and As_2Se_3 were reported by Zallen *et al.*[14] The maximum value of observed splitting is 6 cm^{-1}, which is well beyond the limit of experimental uncertainty. However, in the absence of a clear knowledge of the displacement vectors of the (B_u,A_g) pair, it is difficult to make a systematic calculation.

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