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Optical phonons in mixed-layer crystals of the series SnS_xSe_{2-x} $(0 \le x \le 2)$

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The optical phonons in mixed-layer crystals of the series SnS_xSe_{2-x} $(0 \le x \le 2)$ are calculated theoretically utilizing the effect of the interlayer and intralayer coupling parameters. A two-mode type of behavior is predicted. Long-wavelength optical phonons have been studied for $SnSe_2$, SnS_2, and different solid solutions of SnS_xSe_{2-x}. A satisfactory agreement has been found between theory and experiment.

Mixed crystals of the title series SnS_xSe_{2-x}, where $0 \le x \le 2$ belong to an important class of materials called "layered compounds"[1] in which the bonding within the layer is considerably stronger than the bonding perpendicular to it. The study of such materials is motivated by curiousity as to what extent these compounds may be considered as two-dimensional crystals. The end members of the series (SnS_2 and $SnSe_2$) have been studied extensively earlier by Raman and ir spectroscopy. Their Raman spectra have been reported by Smith *et al.*,[2] Mead and Irwin,[3] and Nakashima *et al.*,[4] and ir reflectivity by Lucovsky *et al.*[5] and Kohler and Becker.[6] But very few experimental results are available at present for other members of the series, i.e., crystals with $0 \le x \le 2$.[7]

Recently Garg[8] has reported the successful growth of large single crystals of $SnSe_2$, SnS_2, and seven different solid solutions of SnS_xSe_{2-x} and the study of their long-wavelength optical phonons by Raman and ir spectroscopy to establish the mode behavior for the series.

Until now, to our knowledge, no theoretical model has been developed which could explain the established mode behavior observed experimentally in SnS_xSe_{2-x}. This paper reports for the first time a theoretical model developed to explain the mode behavior in layered compounds. The application of the present model gives a satisfactory agreement between theory and experiment for the phonon frequencies of SnS_xSe_{2-x}.

The semiconducting layer compound SnX_2 (X=S,Se) crystallize in a lattice having CdI_2 structure[2] (space group D^3_{3d}) in which the metal atom is octahedrally connected to the six nearest-neighbor chalcogen atoms (Fig. 1). Thus the unit cell spans only one layer and contains one molecular unit SnX_2, i.e., three atoms. Thus, there are nine vibrational modes, which are represented by the following irreducible representations of the point group at the center of the Brillouin zone:

$$\Gamma = A_{1g} + 2A_{2u} + E_g + 2E_u \ .$$

The acoustic modes are A_{2u} and E_u, so that there are four optic modes, two Raman-active modes A_{1g} and E_g, and two ir active modes A_{2u} and E_u. To explain the above vibrational modes for SnX_2 on the basis of the Delauney angular force model, the dynamical matrix can be written as

$$\begin{vmatrix} P - mw^2 & Q & R \\ Q & S - Mw^2 & T \\ R & T & U - mw^2 \end{vmatrix} = 0 \ , \qquad (1)$$

where M is the mass of the metal ion and m is the mass of chalcogen atom (S,Se). P, Q, R, S, T, and U are 3×3 dynamical matrices for the CdI_2 structure, which can be written in terms of the angular (α_1', α_2') and radial (α_1, α_2) force constants and the lattice parameters a and c. These are given in the Appendix.

The values of the force constants are calculated by substituting the experimental optical-phonon frequencies of the SnS_2 and $SnSe_2$ systems, respectively, at the zone center.[2] The matrix (1) is then computed to get the phonon behavior of the layered system. The one-mode behavior for SnS_xSe_{2-x} is studied from the above matrix by considering the linear variation of the force constants, lattice constants, and masses of the chalcogen ions.[9] The agreement obtained with the experiment for one-mode behavior is rather poor.

We have, therefore, predicted a two-mode behavior for the mixed-layered SnS_xSe_{2-x} system. From Fig. 1, it is clear that the unit cell spans only one layer and contains one molecular unit SnX_2 (X=S,Se), i.e., three atoms. In Fig. 1, a Sn atom is shown as a solid circle and an X (S,Se) atom by an open circle. SnS_2 and $SnSe_2$ are miscible in

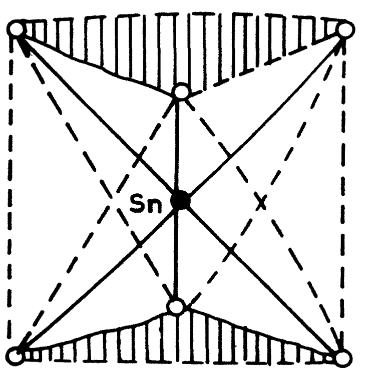

FIG. 1. Octahedral coordination of layers in the crystal structure of SnX_2.

all proportions and form a complete range of binary solid solutions SnS_xSe_{2-x} $(0\leq x\leq 2)$. Therefore it is expected that the sulfur and selenium atoms distribute themselves randomly in the anion lattice sites in such a way that half of the sulfur atoms $(x/2)$ are in the upper layer and half are in the lower layer. Similarly half of the selenium atoms $[(2-x)/2]$ are in the upper layer and half are in the lower layer. The vibrational modes for the above randomly distributed system on the basis of Green's-function formalism[10] are the solutions of the equation

$$|\,(\omega^2 m^{\mu}-\phi^{\mu\mu})\delta_{\mu\nu}-c^{\mu}\phi^{\mu\nu}(q)\,|=0\ . \tag{2}$$

In a mixed-layered crystal of the type SnS_xSe_{2-x} $(0\leq x\leq 2)$ for the upper layer, we have

$$C^{S(u)}=\frac{x}{2},\quad C^{Se(u)}=\frac{2-x}{2},\quad C^{Sn}=1$$

and

$$M^{S(u)}=\frac{2m}{x},\quad M^{Se(u)}=\frac{2m}{2-x},\quad M^{Sn}=M\ ,$$

where u stands for the upper layer. Similarly for the lower layer we have

$$C^{Sn}=1,\quad C^{Se(l)}=\frac{2-x}{2},\quad C^{S(l)}=\frac{x}{2}\ ,$$

$$M^{Sn}=M,\quad M^{Se(l)}=\frac{2m}{2-x},\quad C^{S(l)}=\frac{2m}{x}\ ,$$

where l stands for the lower layer. Also

$$\phi^{S(u)-S(u)}(q)=\frac{x}{2}P,\quad \phi^{Se(u)-Se(u)}(q)=\frac{2-x}{2}P,\quad \phi^{Sn-Sn}(q)=S\ ,$$

$$\phi^{Se(l)-Se(l)}(q)=\frac{2-x}{2}U,\quad \phi^{S(l)-S(l)}(q)=\frac{x}{2}U\ ,$$

$$\phi^{S(u)-Se(u)}(q)=\frac{x}{2}P,\quad \phi^{S(u)-Sn}(q)=Q,\quad \phi^{S(l)-Se(u)}(q)=\frac{x}{2}R,\quad \phi^{S(l)-S(u)}(q)=\frac{x}{2}R\ ,$$

$$\phi^{Se(u)-Sn}(q)=Q,\quad \phi^{Se(l)-Se(u)}(q)=\frac{2-x}{2}R,\quad \phi^{Se(l)-S(u)}(q)=\frac{x}{2}R\ ,$$

$$\phi^{Sn-Se(l)}(q)=T,\quad \phi^{Sn-S(l)}(q)=T,\quad \phi^{Se(u)-S(l)}(q)=\frac{2-x}{2}R\ .$$

Substituting in Eq. (2) we get the dynamical matrix for the mixed system of the order 15×15 as given by Eq. (3);

$$\begin{vmatrix}
\frac{x^2}{4}P-mw^2 & \frac{x(2-x)}{4}P & \frac{x}{2}Q & \frac{x(2-x)}{4}R & \frac{x^2}{4}R \\
\frac{x(2-x)}{4}P & \frac{(2-x)^2}{4}P-mw^2 & \frac{2-x}{2}Q & \frac{(2-x)^2}{4}R & \frac{x(2-x)}{4}R \\
\frac{x}{2}Q & \frac{2-x}{2}Q & S-Mw^2 & \frac{2-x}{2}T & \frac{x}{2}T \\
\frac{x(2-x)}{4}R & \frac{(2-x)^2}{4}R & \frac{2-x}{2}T & \frac{(2-x)^2}{4}U-mw^2 & \frac{x(2-x)}{4}U \\
\frac{x^2}{4}R & \frac{x(2-x)}{4}R & \frac{x}{2}T & \frac{x(2-x)}{4}U & \frac{x^2}{4}U-mw^2
\end{vmatrix}=0\ , \tag{3}$$

where as for the end member unit SnS_2 at $x=2$ and for $SnSe_2$ at $x=0$ the dynamical matrix [Eq. (3)] reduces to Eq. (1).

On analyzing Eq. (3), we find that it exhibits one-mode behavior for all values of x. It is not the case in general, that the exact half of the sulfur atom $(x/2)$ is in the upper layer and that the other half is in the lower layer; similarly, in the practical case half of the selenium atom $[(2-x)/2]$ is not in the upper layer and the other half is not in the lower layer. Actually a part of the sulfur atom is in one layer and the rest is in the other layer and, similarly, a part of the selenium atom is in one layer and the remaining part is in the other layer. To describe these types of interactions we have introduced two coupling constants λ_1 and λ_2 known as the interlayer and the intralayer coupling constants. Therefore,

$$\begin{vmatrix}
\frac{x}{2}\left[\frac{x}{2}+\frac{2-x}{2}\lambda_1\right]P-mw^2 & \frac{x(2-x)(1-\lambda_1)}{4}P & \frac{x}{2}Q & \frac{(1-\lambda_2)x(2-x)}{4}R & \frac{x}{2}\left[\frac{x}{2}+\frac{2-x}{2}\lambda_2\right]R \\
\frac{(1-\lambda_1)x(2-x)}{4}P & \frac{2-x}{2}\left[\frac{2-x}{2}+\frac{x}{2}\lambda_1\right]P-mw^2 & \frac{2-x}{2}Q & \frac{2-x}{2}\left[\frac{2-x}{2}+\frac{x}{2}\lambda_2\right]R & \frac{(2-x)x(1-\lambda_2)}{4}R \\
\frac{x}{2}Q & \frac{2-x}{2}Q & S-Mw^2 & \frac{2-x}{2}T & \frac{x}{2}T \\
\frac{(2-x)x(1-\lambda_2)}{4}R & \frac{2-x}{2}\left[\frac{2-x}{2}+\frac{x}{2}\lambda_2\right]R & \frac{2-x}{2}T & \frac{2-x}{2}\left[\frac{2-x}{2}+\frac{x}{2}\lambda_1\right]U-mw^2 & \frac{(2-x)x(1-\lambda_1)}{4}U \\
\frac{x}{2}\left[\frac{x}{2}+\frac{2-x}{2}\right]R & \frac{x(2-x)(1-\lambda_2)}{4}R & \frac{x}{2}T & \frac{(1-\lambda_1)x(2-x)}{4}U & \frac{x}{2}\left[\frac{x}{2}+\frac{2-x}{2}\lambda_1\right]U-mw^2
\end{vmatrix}=0\ . \tag{4}$$

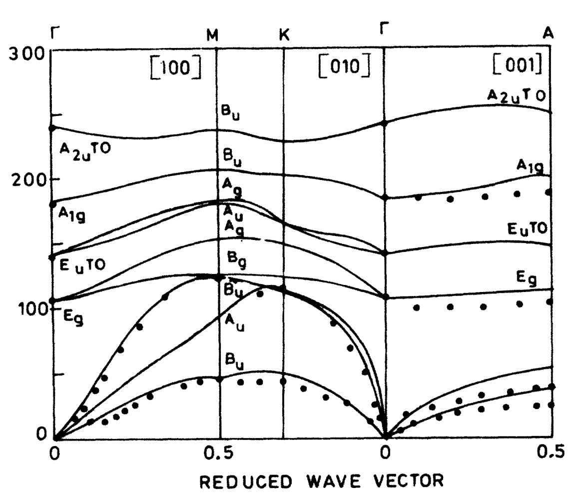

FIG. 2. Phonon dispersion relations of $SnSe_2$. The solid circle shows the experimental points (Ref. 11) and the lines show the calculations using the Delauney angular force model.

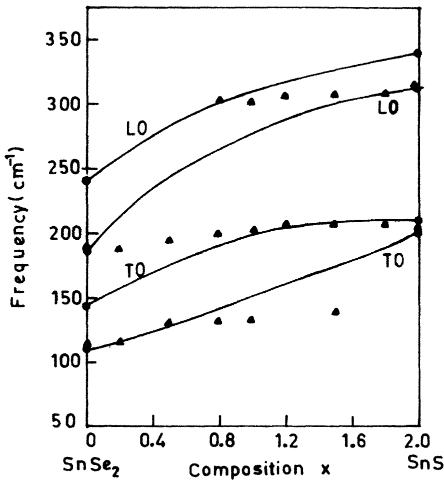

FIG. 4. One-mode behavior in the SnS_xSe_{2-x} layer compound. The experimental points are from Raman spectra (Ref. 8).

The $(x/2)$ S atom will interact with the $(x/2)$ S atom as well as with a $[(2-x)/2]\lambda_1$ Se atom in a layer. Similarly the $[(2-x)/2]$ Se atom will interact with the $[(2-x)/2]$ Se atom as well as with the $(x/2)\lambda_1$ S atom. The case for the coupling constant λ_2 is similar. Thus the dynamical matrix for the mixed system will be given by Eq. (4). It will give two-mode behavior (four sets of optical-phonon frequencies) for all values of x lying between $0 \leq x \leq 2$, and for λ_1 and λ_2 equal to zero and for $x=0$ or $x=2$ Eq. (4) again reduces to Eq. (1).

Figures 2 and 3 exhibit the phonon dispersion relations of $SnSe_2$ and SnS_2 along the principal symmetry directions. In Fig. 2, we also display the experimental points of inelastic neutron scattering measurements by Harbec *et al.*[11] The theoretical curves show a good agreement with the experimental points, except in the [100] direction where the theoretical curves are slightly higher than the experimental points as we have not considered the van der Waals forces between the ions in our model. Similarly in Fig. 3, we exhibit the phonon dispersion of SnS_2 and also the experimental points at the zone boundary from Raman and infrared spectra of Smith *et al.*[2] Figures 4 and 5 display the one-mode and two-mode behavior of the mixed-layer SnS_xSe_{2-x} system.

In Fig. 4, we show four optical-phonon frequencies for the whole range of composition. Experimental points from the Raman spectra of Garg[8] are also shown for the whole range of composition. It is observed that there is a large discrepancy between the Raman phonon frequencies and the theoretically calculated frequencies. It is well known that most of the solid solutions behave in one of the three distinct types, namely, one-mode, two-mode,

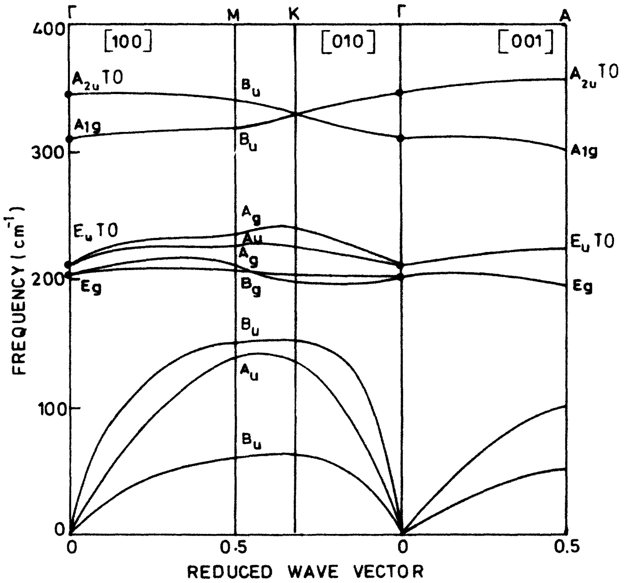

FIG. 3. Phonon dispersion relations of SnS_2. Experimental points at the zone boundary from Raman and ir spectra of Smith *et al.* (Ref. 2) are also shown as solid circles.

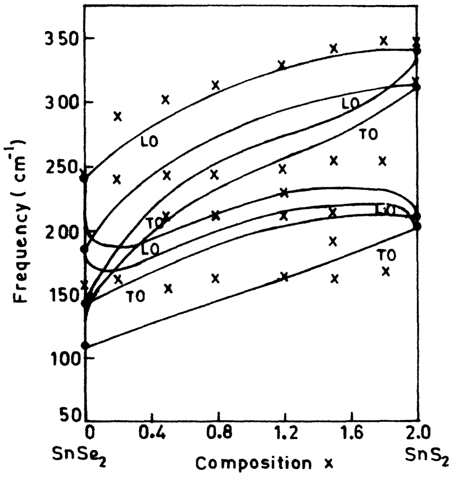

FIG. 5. Two-mode behavior in SnS_xSe_{2-x} as a function of composition. Experimental points are from ir spectra (Ref. 8).

and mixed-mode behavior (Nayak and Behra).[12] According to Chang and Mitra[13] several criteria have been developed which can give some indication of the type of mode behavior expected from a given solid solution. It is expected that the mixed layered system $\mathrm{SnS}_x\mathrm{Se}_{2-x}$ may not be a case for any of these criteria; because of its extreme anisotropy for these materials the relationship of masses alone is not sufficient. In the solid solution $\mathrm{SnS}_x\mathrm{Se}_{2-x}$ the substitution is of the higher element and the mass of sulfur is less than the reduced mass of SnSe_2. These facts indicate that the two-mode behavior may be expected here. The two-mode analysis of $\mathrm{SnS}_x\mathrm{Se}_{2-x}$ is presented in Fig. 5. Experimental points from the ir-active modes[8] of $\mathrm{SnS}_x\mathrm{Se}_{2-x}$ are also shown in Fig. 5. A satisfactory agreement has been obtained between the theory and the experiment. Thus it is evident that the $\mathrm{SnS}_x\mathrm{Se}_{2-x}$ $(0 \leq x \leq 2)$ system does not display one-mode–type behavior. We infer that the behavior appears to be a two-mode type.

APPENDIX

The matrix elements for the dynamical matrix Eq. (1) are written as, for upper-layer chalcogen atom as the origin,

$$D\begin{bmatrix}1 & 1\\ x & x\end{bmatrix} = 3\alpha_1' + \frac{a^2}{2A^2}(\alpha_1-\alpha_1') + 6\alpha_2' + \frac{a^2}{B^2}(\alpha_2-\alpha_2') \ ,$$

$$D\begin{bmatrix}1 & 1\\ x & y\end{bmatrix} = D\begin{bmatrix}1 & 1\\ x & z\end{bmatrix} = 0 \ ,$$

$$D\begin{bmatrix}1 & 2\\ x & x\end{bmatrix} = -\alpha_1' e^{-i((c/4)q_3)}\left[e^{-i(a/\sqrt{3})q_2} + 2\cos\frac{a}{2}q_1 e^{i(a/2\sqrt{3})q_2}\right] - \frac{a^2}{2A^2}(\alpha_1-\alpha_1')\cos\frac{a}{2}q_1 e^{-i(-(a/2\sqrt{3})q_2+(c/4)q_3)} \ ,$$

$$D\begin{bmatrix}1 & 2\\ x & y\end{bmatrix} = -i\frac{a^2}{2(3)^{1/2}A^2}(\alpha_1-\alpha_1')e^{i(a/2\sqrt{3})q_2}\sin\frac{a}{2}q_1 e^{-i(c/4)q_3} \ ,$$

$$D\begin{bmatrix}1 & 2\\ x & z\end{bmatrix} = i\frac{ac}{4A^2}(\alpha_1-\alpha_1')e^{i(a/2\sqrt{3})q_2}\sin\frac{a}{2}q_1 e^{-i(c/4)q_3} \ ,$$

$$D\begin{bmatrix}1 & 3\\ x & x\end{bmatrix} = -2\alpha_2' e^{i(a/\sqrt{3})q_2}\cos\frac{c}{2}q_3 - \left[\alpha_2' + \frac{a^2}{4B^2}(\alpha_2-\alpha_2')\right]e^{-i(a/2\sqrt{3})q_2}\cos\frac{a}{2}q_1\cos\frac{c}{2}q_3 \ ,$$

$$D\begin{bmatrix}1 & 3\\ x & y\end{bmatrix} = i\frac{a^2}{(3)^{1/2}B^2}(\alpha_2-\alpha_2')e^{-i(a/2\sqrt{3})q_2}\cos\frac{c}{2}q_3\sin\frac{a}{2}q_1 \ ,$$

$$D\begin{bmatrix}1 & 3\\ x & z\end{bmatrix} = -\frac{ac}{B^2}(\alpha_2-\alpha_2')e^{i(a/2\sqrt{3})q_2}\sin\frac{c}{2}q_2\sin\frac{a}{2}q_1 \ ,$$

$$D\begin{bmatrix}1 & 1\\ y & x\end{bmatrix} = 0 \ ,$$

$$D\begin{bmatrix}1 & 1\\ y & y\end{bmatrix} = D\begin{bmatrix}1 & 1\\ x & x\end{bmatrix} \ ,$$

$$D\begin{bmatrix}1 & 1\\ y & z\end{bmatrix} = 0 \ ,$$

$$D\begin{bmatrix}1 & 2\\ y & x\end{bmatrix} = D\begin{bmatrix}1 & 2\\ x & y\end{bmatrix}, \quad D\begin{bmatrix}1 & 2\\ y & y\end{bmatrix} = D\begin{bmatrix}1 & 2\\ x & x\end{bmatrix} \ ,$$

$$D\begin{bmatrix}1 & 2\\ y & z\end{bmatrix} = -\frac{ac}{4(3)^{1/2}A^2}(\alpha_1-\alpha_1')e^{-i((a/\sqrt{3})q_2+(c/4)q_3)} + \frac{ac}{4(3)^{1/2}A^2}(\alpha_1-\alpha_1')e^{-i(-(a/2\sqrt{3})q_2+(c/4)q_3)}\cos\frac{a}{2}q_1 \ ,$$

$$D\begin{bmatrix}1 & 3\\ y & x\end{bmatrix} = D\begin{bmatrix}1 & 3\\ x & y\end{bmatrix} \ ,$$

$$D\begin{bmatrix}1 & 3\\ y & y\end{bmatrix} = -\left[\alpha_2' + \frac{a^2}{3B^2}(\alpha_2-\alpha_2')\right]e^{i(a/\sqrt{3})q_2}2\cos\frac{c}{2}q_3 - \left[\alpha_2' + \frac{a^2}{12B^2}(\alpha_2-\alpha_2')\right]e^{i(a/2\sqrt{3})q_2}4\cos\frac{a}{2}q_1\cos\frac{c}{2}q_3 \ ,$$

$$D\begin{bmatrix}1&3\\y&z\end{bmatrix}=\frac{ac}{4(3)^{1/2}B^2}(\alpha_2-\alpha_2')2e^{i(a/\sqrt{3})q_2}\left[-2i\sin\frac{c}{2}q_3\right]+\frac{ac}{4(3)^{1/2}B^2}(\alpha_2-\alpha_2')e^{-i(a/2\sqrt{3})q_2}2i\sin\frac{c}{2}q_3 2\cos\frac{a}{2}q_1\ ,$$

$$D\begin{bmatrix}1&1\\z&x\end{bmatrix}=D\begin{bmatrix}1&1\\z&y\end{bmatrix}=0\ ,$$

$$D\begin{bmatrix}1&1\\z&z\end{bmatrix}=3\alpha_1'+\frac{3c^2}{16A^2}(\alpha_1-\alpha_1')+6\alpha_2'+\frac{3c^2}{2B^2}(\alpha_2-\alpha_2')\ ,$$

$$D\begin{bmatrix}1&2\\z&x\end{bmatrix}=D\begin{bmatrix}1&2\\x&z\end{bmatrix},\quad D\begin{bmatrix}1&2\\z&y\end{bmatrix}=D\begin{bmatrix}1&2\\y&z\end{bmatrix}\ ,$$

$$D\begin{bmatrix}1&2\\z&z\end{bmatrix}=\left[-\alpha_1'+\frac{c^2}{16A^2}(\alpha_1-\alpha_1')\right]\left[e^{(-i(a/\sqrt{3})q_2+(c/4)q_3)}+2e^{-i((a/2\sqrt{3})q_2+(c/4)q_3)}\cos\frac{a}{2}q_1\right]\ ,$$

$$D\begin{bmatrix}1&3\\z&x\end{bmatrix}=D\begin{bmatrix}1&3\\x&z\end{bmatrix},\quad D\begin{bmatrix}1&3\\z&y\end{bmatrix}=D\begin{bmatrix}1&3\\y&z\end{bmatrix}\ ,$$

$$D\begin{bmatrix}1&3\\z&z\end{bmatrix}=\left[-\alpha_2'+\frac{c^2}{4B^2}(\alpha_2-\alpha_2')\right]\left[2e^{i(a/\sqrt{3})q_2}\cos\frac{c}{2}q_3+4e^{-i(a/2\sqrt{3})q_2}\cos\frac{a}{2}q_1\cos\frac{c}{2}q_3\right]\ .$$

For Sn as the origin,

$$D\begin{bmatrix}2&1\\x&x\end{bmatrix}=D^*\begin{bmatrix}1&2\\x&x\end{bmatrix},\quad D\begin{bmatrix}2&1\\x&y\end{bmatrix}=D^*\begin{bmatrix}1&2\\x&y\end{bmatrix},\quad D\begin{bmatrix}2&1\\x&z\end{bmatrix}=D^*\begin{bmatrix}1&2\\x&z\end{bmatrix}\ ,$$

$$D\begin{bmatrix}2&2\\x&x\end{bmatrix}=6\alpha_1'+\frac{a^2}{A^2}(\alpha_1-\alpha_1')\ ,$$

$$D\begin{bmatrix}2&2\\x&y\end{bmatrix}=0,\quad D\begin{bmatrix}2&2\\x&z\end{bmatrix}=0\ ,$$

$$D\begin{bmatrix}2&3\\x&x\end{bmatrix}=D\begin{bmatrix}1&2\\x&x\end{bmatrix},\quad D\begin{bmatrix}2&3\\x&y\end{bmatrix}=D\begin{bmatrix}1&2\\x&y\end{bmatrix},\quad D\begin{bmatrix}2&3\\x&z\end{bmatrix}=D\begin{bmatrix}1&2\\x&z\end{bmatrix}\ ,$$

$$D\begin{bmatrix}2&1\\y&x\end{bmatrix}=D\begin{bmatrix}2&1\\x&y\end{bmatrix},\quad D\begin{bmatrix}2&1\\y&y\end{bmatrix}=D^*\begin{bmatrix}1&2\\y&y\end{bmatrix},\quad D\begin{bmatrix}2&1\\y&z\end{bmatrix}=D^*\begin{bmatrix}1&2\\y&z\end{bmatrix}\ ,$$

$$D\begin{bmatrix}2&2\\y&y\end{bmatrix}=D\begin{bmatrix}2&2\\x&x\end{bmatrix},\quad D\begin{bmatrix}2&2\\y&x\end{bmatrix}=0,\quad D\begin{bmatrix}2&2\\y&z\end{bmatrix}=0\ ,$$

$$D\begin{bmatrix}2&3\\y&x\end{bmatrix}=D\begin{bmatrix}1&2\\x&y\end{bmatrix},\quad D\begin{bmatrix}2&3\\y&y\end{bmatrix}=D\begin{bmatrix}2&1\\y&y\end{bmatrix},\quad D\begin{bmatrix}2&3\\y&z\end{bmatrix}=D\begin{bmatrix}2&1\\y&z\end{bmatrix}\ ,$$

$$D\begin{bmatrix}2&1\\z&x\end{bmatrix}=D\begin{bmatrix}2&1\\x&z\end{bmatrix},\quad D\begin{bmatrix}2&1\\z&y\end{bmatrix}=D\begin{bmatrix}2&1\\y&z\end{bmatrix},\quad D\begin{bmatrix}2&1\\z&z\end{bmatrix}=D^*\begin{bmatrix}1&2\\x&z\end{bmatrix}\ ,$$

$$D\begin{bmatrix}2&2\\z&x\end{bmatrix}=D\begin{bmatrix}2&2\\z&y\end{bmatrix}=0\ ,$$

$$D\begin{bmatrix}2&2\\z&z\end{bmatrix}=6\alpha_1'+\frac{3c^2}{8A^2}(\alpha_1-\alpha_1')\ ,$$

$$D\begin{bmatrix}2&3\\z&x\end{bmatrix}=D\begin{bmatrix}2&3\\x&z\end{bmatrix},\quad D\begin{bmatrix}2&3\\z&y\end{bmatrix}=D\begin{bmatrix}2&3\\y&z\end{bmatrix},\quad D\begin{bmatrix}2&3\\z&z\end{bmatrix}=D\begin{bmatrix}1&2\\z&z\end{bmatrix}\ .$$

For lower-layer chalcogen atoms as the origin,

$$D\begin{bmatrix}3&1\\x&x\end{bmatrix}=D^*\begin{bmatrix}1&3\\x&x\end{bmatrix}\ ,$$

$$D\begin{bmatrix}3 & 1\\ x & y\end{bmatrix}=D^*\begin{bmatrix}1 & 3\\ x & y\end{bmatrix},$$

$$D\begin{bmatrix}3 & 1\\ x & z\end{bmatrix}=D^*\begin{bmatrix}1 & 3\\ x & z\end{bmatrix},$$

$$D\begin{bmatrix}3 & 2\\ x & x\end{bmatrix}=D^*\begin{bmatrix}1 & 2\\ x & x\end{bmatrix},$$

$$D\begin{bmatrix}3 & 2\\ x & y\end{bmatrix}=D^*\begin{bmatrix}1 & 2\\ x & y\end{bmatrix},$$

$$D\begin{bmatrix}3 & 2\\ x & z\end{bmatrix}=D^*\begin{bmatrix}1 & 2\\ x & z\end{bmatrix},$$

$$D\begin{bmatrix}3 & 3\\ x & x\end{bmatrix}=D\begin{bmatrix}1 & 1\\ x & x\end{bmatrix},\quad D\begin{bmatrix}3 & 3\\ x & y\end{bmatrix}=D\begin{bmatrix}3 & 3\\ x & z\end{bmatrix}=0\,,$$

$$D\begin{bmatrix}3 & 1\\ z & x\end{bmatrix}=D\begin{bmatrix}3 & 1\\ x & z\end{bmatrix},\quad D\begin{bmatrix}3 & 1\\ z & y\end{bmatrix}=D\begin{bmatrix}3 & 1\\ y & z\end{bmatrix},\quad D\begin{bmatrix}3 & 1\\ z & z\end{bmatrix}=D^*\begin{bmatrix}1 & 3\\ z & z\end{bmatrix},$$

$$D\begin{bmatrix}3 & 2\\ z & x\end{bmatrix}=D\begin{bmatrix}3 & 2\\ x & z\end{bmatrix},\quad D\begin{bmatrix}3 & 2\\ z & y\end{bmatrix}=D\begin{bmatrix}3 & 2\\ y & z\end{bmatrix},\quad D\begin{bmatrix}3 & 2\\ z & z\end{bmatrix}=D\begin{bmatrix}1 & 2\\ z & z\end{bmatrix},$$

$$D\begin{bmatrix}3 & 3\\ z & x\end{bmatrix}=0,\quad D\begin{bmatrix}3 & 3\\ z & y\end{bmatrix}=0$$

$$D\begin{bmatrix}3 & 3\\ z & y\end{bmatrix}=D\begin{bmatrix}1 & 1\\ z & z\end{bmatrix},$$

where

$$A=\left[\frac{a^2}{3}+\frac{c^2}{16}\right]^{1/2},\quad B=\left[\frac{a^2}{3}+\frac{c^2}{4}\right]^{1/2},$$

and where

$$D\begin{bmatrix}1 & 1\\ \alpha & \beta\end{bmatrix}$$

are the dynamical matrix elements for the matrix P,

$$D\begin{bmatrix}1 & 2\\ \alpha & \beta\end{bmatrix}$$

are the dynamical matrix elements for the matrix Q,

$$D\begin{bmatrix}1 & 3\\ \alpha & \beta\end{bmatrix}$$

are the dynamical matrix elements for the matrix R,

$$D\begin{bmatrix}2 & 2\\ \alpha & \beta\end{bmatrix}$$

are the dynamical matrix elements for the matrix S,

$$D\begin{bmatrix}2 & 3\\ \alpha & \beta\end{bmatrix}$$

are the dynamical matrix elements for the matrix T, and

$$D\begin{bmatrix}3 & 3\\ \alpha & \beta\end{bmatrix}$$

are the dynamical matrix elements for the matrix U.

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