MREI-model calculations for layered mixed crystals of the series $\text{Hf S}_2-\chi \text{Te}_\chi$ ($0 \leq \chi \leq 2$)

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Optical phonon frequencies for IR active modes have been calculated for layered mixed crystals in the series $\text{Hf S}_2-\chi \text{Te}_\chi$ ($0 \leq \chi \leq 2$) using MREI-model. The model is simple and involves only two adjustable parameters. Various force constants and the values of local and gap modes have been reported. The model has been found to work reasonably well and the calculated values agree with the experimental values.

Keywords: MREI-model, $\text{Hf S}_2-\chi \text{Te}_\chi$, Infrared, Phonon calculations, Layered compounds

1 Introduction

The layered dichalcogenides crystals of group IV transition metals, $\text{MX}_2$($\text{X}=\text{S, Se, Te}$) have been the subject of intense scientific research\(^1\)-\(^3\). One of the important features of these layered materials is their quasi-two dimensional structure. Due to this the anisotropy is revealed through their diverse physical properties. When intercalated with alkali atom or organic molecule these materials show high transition temperature superconducting behaviour\(^4\),\(^5\) and also used as positive electrode in secondary lithium batteries\(^6\),\(^7\). These dichalcogenides generally form solid solutions as per Vegard’s law. Hafnium sulfotelluride is such a mixed series formed by solid solutions of $\text{HfS}_2$ and $\text{HfTe}_2$.

IR reflectivity\(^8\),\(^9\) and Raman scattering\(^10\)-\(^12\) measurements have been reported earlier for the end member $\text{HfS}_2$. The experimental phonon studies on mixed $\text{Hf S}_2-\chi \text{Te}_\chi$ ($0 \leq \chi \leq 2$) system was reported by Kliche G\(^13\) in 1986 using IR reflectivity of pressed pallets. No IR data on single crystals and no Raman data of the mixed crystal system are available in the literature probably due to the difficulty in growing good single crystals of the series. Based on the available experimental data\(^13\) a theoretical study has been reported\(^14\). The lattice dynamical model used in it is relatively complex and utilizes various interlayer and intralayer coupling parameters.

In the present paper, modified random element isodisplacement (MREI) model is applied to calculate the IR mode frequencies of this mixed system. The MREI model was originally proposed for $\text{AB}_1-\chi \text{C}_\chi$ ($0 \leq \chi \leq 1$) type mixed crystals\(^15\). The model was modified for $\text{AB}_2-\chi \text{C}_\chi$ ($0 \leq \chi \leq 2$) type mixed crystals and was found working satisfactorily in $\text{SnS}_2-\chi \text{Se}_\chi$ (Ref. 16) and $\text{TiS}_2-\chi \text{Se}_\chi$ ($0 \leq \chi \leq 2$)\(^17\) crystal systems. The model is a simple model and is physically well acceptable for such layered mixed crystals.

2 Crystal Structure

Members of mixed series $\text{Hf S}_2-\chi \text{Te}_\chi$ ($0 \leq \chi \leq 2$) crystallize in CdI$_2$-type layered structure. Each layer contains $X$-$\text{Hf}$-$X$ sandwich of three sheets in which hafnium atom is octahedrally co-ordinated to six nearest $X$-atoms. Such layers are held together with weak van der Waal inter-layer interaction along the $c$-axis forming AbC: AbC :... stacking sequence. The $2H$-polytype unit cell extends over one layer with a linear triatomic molecular unit. The resulting nine vibrational modes have following irreducible representation at the center of Brillouin zone:

$$\Gamma = A_{1g} + 2A_{2u} + E_{g} + 2E_{u}$$

Here $E$’s are doubly degenerate modes and $A$’s are non-degenerate modes. Out of optic modes, $A_{2u}$ and $E_{u}$ are IR active modes and $A_{1g}$ and $E_{g}$ are Raman active modes. The atomic displacement vectors for IR and Raman active modes of $\text{HfX}_2$ are shown in Fig. 1. In IR modes both $X$ atom sheets vibrate in phase but opposite to $\text{Hf}$ atom sheet. The Raman modes, on the other hand, are identified with $X$ atoms, in the two sheets of the layer, vibrating opposite to each other and the $\text{Hf}$ atoms (being at center of inversion) remain
stationary. The vibration direction in $E$-mode is along the basal plane while that in $A$-mode is along the $c$-axis.

3 Theory

The model utilizes the basic assumptions of isodisplacement and randomness. The isodisplacement proposes that the atoms of same type vibrate as a rigid unit and the randomness suggests that the vibration is under the influence of statistical average of neighbouring atoms of different type. The macroscopic electric field term which leads to LO-TO splitting is omitted in the model for the time being. In HfS$_2$-$x$Te$_x$ ($0 \leq x < 2$) system the IR frequencies are available experimentally but no Raman data has been reported so far for $0 < x \leq 2$. This restricted the present calculations to IR active modes only. Under these assumption for IR active modes following boundary conditions are obtained:

at $x = 0$

$$\omega_{s} = \left( \frac{1}{m_{sS}} \right)^{1/2} = \omega_{i}(\text{HfS}_2) \quad \ldots(1)$$

$$\omega = \left( \frac{1}{m_{sS}} \left( F_{01} + 2F_{02} \right) \right)^{1/2} = \omega_{i}(\text{HfS}_2) \quad \ldots(2)$$

$$\omega = \left( \frac{1}{m_{sS}} \left( 1 - 2\theta \right) \right)^{1/2} = \omega_{i}(\text{HfS}_2) \quad \ldots(3)$$

$$\omega = \left( \frac{1}{m_{sS}} \left( 1 - 2\theta \right) \right)^{1/2} = \omega_{i}(\text{HfS}_2) \quad \ldots(4)$$

Eqs (1) and (4) are the TO mode frequencies of end members HfS$_2$ and HfTe$_2$ whereas, Eqs (2) and (3) represent their impurity modes in the low concentration region of Te and S atoms, respectively.

The equation for IR active mode frequency is

$$\omega^2 = 0.5(1 - \theta x)F_{01} \left[ \frac{2 - x}{m_{Hf}} + \frac{1}{m_{S}} \right] + F_{02} \left[ \frac{x}{m_{S}} + \frac{2 - x}{m_{Te}} \right]$$

$$+ F_{03} \left[ \frac{x}{m_{Hf}} + \frac{1}{m_{Hf}} \right] + F_{03} \left[ \frac{x}{m_{Hf}} + \frac{1}{m_{Hf}} \right] + F_{03} \left[ \frac{x}{m_{Hf}} + \frac{1}{m_{Hf}} \right]$$

$$+ 4x(2 - x) \left( \frac{F_{03}}{m_{Hf}} - \frac{F_{02}}{m_{Hf}} \right) \left( \frac{F_{01}}{m_{Hf}} - \frac{F_{02}}{m_{Hf}} \right) \ldots(5)$$

The values of $\omega$, for a given $x$ ($0 < x < 2$) can be calculated from Eq. (5), if the four unknowns $F_{01}$, $F_{02}$, $F_{03}$ and $\theta$ can be determined from Eqs (1)-(4). In these equations $\omega_{i}(\text{HfS}_2)$ and $\omega_{i}(\text{HfTe}_2)$ are not available experimentally. Some starting values (estimated from extrapolated values) are assigned to these $\omega_{i}$’s and the phonon mode frequencies are determined using the model, for each composition of mixed crystals. The sum of squares of deviations of these values from corresponding experimentally reported values (at room temperature) is then obtained. The floating parameters (the two $\omega_{i}$’s) are now adjusted by continuous iteration to achieve the condition of least square deviation. Thus the final set of the force constants and impurity modes is obtained. The IR active phonon modes frequencies for this type of mixed crystal series can now be calculated for each composition ($0 < x < 2$).

4 Results and Discussion

The optically active phonon mode frequencies for both ($E_u$ and $A_{2u}$) IR active modes have been
calculated for layered crystals of mixed Hf S$_{2-x}$Tex ($0 \leq x \leq 2$) series, using experimental IR data available for end members$^{13}$. The method of least square deviation is used to get the result, best fitted with the corresponding experimental frequencies$^{13}$ for other members of the series.

The phonon frequencies thus obtained are plotted against the composition parameter $x$ in Fig. 2. The continuous curves represent theoretical results. Earlier reported experimental data (marked by *) and theoretical curves (shown by ---) have also been included in the figure to make a comparison easier. The root-mean-square deviation of theoretically calculated values of IR frequencies from corresponding experimental values are 13.87 and 24.16 cm$^{-1}$ respectively for $A_{2u}$ and $E_u$ modes. The values of various force constants used in the model for each mode are listed in Table 1 along with the local and gap mode frequencies.

In Fig. 2, two types of experimental frequencies marked by * and o are plotted. The points marked by o represent the plasmon mode which are not used in fitting of the MREI model calculated phonon frequencies. Only* marked points are used. Fig. 2 clearly reveals that the results for IR phonon

### Table 1 — MREI model parameters for Hf S$_{2-x}$Tex ($0 \leq x \leq 2$) mixed series

<table>
<thead>
<tr>
<th></th>
<th>$F_{01} \times 10^6$ amu cm$^{-2}$</th>
<th>$F_{02} \times 10^6$ amu cm$^{-2}$</th>
<th>$F_{03} \times 10^6$ amu cm$^{-2}$</th>
<th>$\theta$</th>
<th>$\omega_i$(HfS$_2$) cm$^{-1}$</th>
<th>$\Omega_i$(HfTe$_2$) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{2u}$</td>
<td>2.57</td>
<td>0.33</td>
<td>1.66</td>
<td>0.095</td>
<td>135</td>
<td>286</td>
</tr>
<tr>
<td>$E_u$</td>
<td>0.65</td>
<td>0.71</td>
<td>0.44</td>
<td>-0.089</td>
<td>121</td>
<td>276</td>
</tr>
</tbody>
</table>

### Table 2 — IR mode frequencies (in cm$^{-1}$) of layered crystal of Hf S$_{2-x}$Tex ($0 \leq x \leq 2$) mixed series

<table>
<thead>
<tr>
<th>$x$</th>
<th>$A_{2u}$ mode of HfTe$_2$</th>
<th>$E_u$ mode of HfS$_2$</th>
<th>$A_{2u}$ mode of HfTe$_2$</th>
<th>$A_{2u}$ mode of HfS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>A</td>
</tr>
<tr>
<td>0</td>
<td>124$^*$</td>
<td>—</td>
<td>121</td>
<td>166</td>
</tr>
<tr>
<td>0.2</td>
<td>120</td>
<td>120</td>
<td>116</td>
<td>168</td>
</tr>
<tr>
<td>0.4</td>
<td>124</td>
<td>118</td>
<td>113</td>
<td>189</td>
</tr>
<tr>
<td>0.6</td>
<td>112</td>
<td>117</td>
<td>111</td>
<td>205</td>
</tr>
<tr>
<td>0.8</td>
<td>109</td>
<td>116</td>
<td>109</td>
<td>211</td>
</tr>
<tr>
<td>1.0</td>
<td>105</td>
<td>115</td>
<td>107</td>
<td>225</td>
</tr>
<tr>
<td>1.2</td>
<td>101</td>
<td>113</td>
<td>105</td>
<td>231</td>
</tr>
<tr>
<td>1.4</td>
<td>101</td>
<td>112</td>
<td>104</td>
<td>250</td>
</tr>
<tr>
<td>1.5</td>
<td>99</td>
<td>—</td>
<td>103</td>
<td>248</td>
</tr>
<tr>
<td>1.6</td>
<td>100</td>
<td>—</td>
<td>103</td>
<td>265</td>
</tr>
<tr>
<td>1.7</td>
<td>100</td>
<td>110</td>
<td>102</td>
<td>270</td>
</tr>
<tr>
<td>1.8</td>
<td>102</td>
<td>116</td>
<td>101</td>
<td>—</td>
</tr>
<tr>
<td>1.9</td>
<td>102</td>
<td>—</td>
<td>101</td>
<td>—</td>
</tr>
<tr>
<td>2.0</td>
<td>100$'$</td>
<td>128</td>
<td>100$'$</td>
<td>—</td>
</tr>
</tbody>
</table>

$^*$: Plasmon modes, not used in fitting of calculated values; $^*$: Extrapolated values from Ref 13; A: Ref 13; B: Ref 14; C: Present MREI model calculations.
frequencies of both $E_u$ and $A_{2u}$ modes obtained from the present relatively simple model are better as compared to those calculated from earlier theoretical model. In earlier theoretical work a some experimental points of Kliche G 13 have not been shown properly which is clearly evident from Table 2. The frequency curves of earlier work show rise and fall in frequency at the end $x=0$ and $x=2$, which is against the reported experimental behaviour.

The calculated values of local and gap mode frequencies are 286 and 121 cm$^{-1}$ respectively which are close to the previous predicted values. The order of magnitudes of various intralayer force constants is $10^6$ amu cm$^{-2}$ which is consistent with those reported for similar materials.

5 Conclusions

The MREI model has been found to work quite satisfactorily in mixed layer crystal system Hf S$_{2-x}$Te$_x$ ($0 \leq x \leq 2$). The results calculated for IR frequencies using this simple model are in close agreement with reported experimental values. The frequencies of local and gap modes obtained from this model agree with their corresponding predicted values. The values of various force constants obtained are consistent with those reported earlier for similar layered materials.

References