

Effect of van der Waals and three body interactions on the lattice dynamics of Ionic crystals: an application to SrO

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ABSTRACT : A new model of lattice dynamics has been developed by incorporating the effect of van der Waals interactions and three-body interactions in the frame work of rigid shell model where short range interactions are effective upto the second neighbour. This model has been applied to study the complete lattice dynamics of strontium oxide (SrO). A good agreement has been obtained between theory and experiment.

Keywords: Lattice dynamics, Phonon dispersion curves, Debye temperature, two phonon IR and Raman Spectra, An harmonic elastic constants, combined density of states, strontium oxide.

I. INTRODUCTION

The present paper is an outcome to the efforts devoted to carry out a systematic theoretical investigation of the phonon dispersion, Debye temperature variation, two phonon density of states and third and fourth order elastic constants and present derivatives of SrO. The inputs for undertaking this work was gained from the fact that the oxides of alkaline earths form an important class of ionic solid with NaCl structure which possess peculiar elastic and dielectric properties. This is self evident from the fact that the experimental elastic constants obey the strange relation ($C_{44} \approx 2C_{12}$) for MgO. Also the static and high frequency dielectric constants for these solids have much higher values than the alkali halides. The lattice dynamic of these solids has been extensively studied both theoretically and experimentally during the recent past. The experimental measurements have provided a wealth of data on their phonon dispersion, elastic and dielectric properties. In order to interpret them, several lattice dynamical models have been use namely, the rigid ion model (RIM) [1], the rigid shell model (RSM) [2] and some other variations of the shell model [3 and 4], and however, none of them has been able to predict the experimental results very well. The strange features in the nature and physical properties of the alkaline earth oxides (MgO, CaO, SrO and BaO) have given an increased interest in study of their lattice dynamics. Although, the dispersion relations deduced from the neutron scattering techniques are available for the all of the them [5-9] and their interpretations by means of theoretical models [10-16] have also met with great success, still, the studies of lattice dynamics of SrO has been problem yet to be discussed.

In order to explain the lattice vibrational behaviour of use better, the present authors have developed a model VTSM which includes the effects of van der Walls interactions (VWI) and three-body interactions (TBI) in the frame work of both ions polarizable rigid shell model (RSM). In this model second neighbour short range interactions have been considered to be effective upto the second neighbours.

II. THEORY

In addition to the Coulomb attraction force, there exists another attraction between the closed shell atoms. The nature of this attraction is different and owes its origin to the correlations of the electron motions in different atoms. The electrons of each atom shift with respect to the nucleus in the presence of other atoms and consequently an atom becomes an electric dipole. The instantaneous dipole moment of a closed shell atom induces a dipole moment on a similar atom and the interactions energy thus arising is known as the van der Waals interaction (VWI) potential. Now including the effects of van der Waals interactions and three-body interactions in the frame work of both ions polarizable rigid shell model (RSM), the general formalism of present model (VTSM) can be derived from the crystal potential whose relevant expression per unit cell is given by

$$\phi = \phi^C + \phi^R + \phi^{TBI} + \phi^{VWI} \quad (1)$$

where, first term ϕ^C is Coulomb intersection potential and is long-range in nature. Second term ϕ^R is short range overlap repulsion potential. Third term ϕ^{TBI} is three body interactions potential and the last term ϕ^{VWI} is van der Waals interaction potential and owes its origin to the correlations of the electron motions in different atoms.

Using the crystal expression (1) and introducing the effect of VWI and TBI, the secular determinant:

$$|\underline{D}(\bar{q}) - W^2 \underline{m} \underline{I}| = 0 \quad (2)$$

For the frequency determination here $\underline{D}(q)$ is the (6×6) dynamical matrix given by

$$\begin{aligned} \underline{D}(\bar{q}) = & (\underline{R} + \underline{Z}_m \underline{C}' \underline{Z}_m) - (\underline{T} + \underline{Z}_m \underline{C}' \underline{Y}_m) \\ & \times (\underline{S} + \underline{K} + \underline{Y}_m \underline{C}' \underline{Y}_m)^{-1} \times (\underline{T}^T + \underline{Y}_m \underline{C}' \underline{Z}_m) \end{aligned} \quad (3)$$

The number of adjustable parameters have been largely reduced by considering all the short-range interactions to act only through the shells. This assumptions leads to $\underline{R} = \underline{T} = \underline{S} \cdot \underline{C}'$ is the modified long-range interaction matrix given by

$$\underline{C}' = \underline{C} + (\underline{Z}_m^{-2} 2r_0 f'_0) \underline{r} \quad (4)$$

and the expressions derived for elastic constants from eqn. (4) corresponding to present model are obtained as

$$\frac{4r_0^4}{e^2} C_{11} = \left[-5.112\xi^2 + A_{12} + \frac{1}{2}(A_{11} + A_{22}) + \frac{1}{2}(B_{11} + B_{22}) + 9.3204\xi'^2 \right] \quad (5)$$

$$\frac{4r_0^4}{e^2} C_{12} = \left[0.226\xi^2 - B_{12} + \frac{1}{4}(A_{11} + A_{22}) - \frac{5}{4}(B_{11} + B_{22}) + 9.3204\xi'^2 \right] \quad (6)$$

$$\frac{4r_0^4}{e^2} C_{44} = \left[2.556\xi^2 + B_{12} + \frac{1}{4}(A_{11} + A_{22}) + \frac{3}{4}(B_{11} + B_{22}) \right] \quad (7)$$

In view of the equilibrium condition $[d\phi/dr]_0 = 0$

$$\text{or } B_{11} + B_{22} + B_{12} = -1.165\xi^2 \quad (8)$$

$$\text{where } \xi = \pm \sqrt{\left\{ 1 + \frac{12f(r)}{z} \right\}_0}, \quad \xi' = \pm \sqrt{\left\{ \frac{r}{z} \cdot \frac{df}{dr} \right\}_0} \quad (9)$$

$$\text{and } Z_m = Z \xi$$

The term $f(r)$ is a function dependent on the overlap integrals of the electron wave functions and the subscript zero on the brackets indicates the equilibrium values of the quantities inside. The expression (7) can now be written in the form

$$\frac{4r_0^4}{e^2} C_{44} = \left[1.391\xi^2 + \frac{A_2 - B_2}{4} \right] \quad (10)$$

As C_{44} is a very small quantity in the present case, the calculated value of $[(4r_0^4 / e^2)C_{44} - 1.391\xi^2]$ is found to be a negative quantity so that $(A_2 - B_2)$ is negative. This suggests that these terms belong to an attractive interaction and possibly arise due to van der Waals energy. The van der Waals energy converges fast but the overlap repulsion converges much faster. Therefore the overlap repulsion is effective only upto the first neighbour and the van der Waals attraction upto the second neighbour.

If we consider the second neighbour dipole-dipole van der Waals interaction energy, then it is expressed as

$$\phi_{dd}^{VWI}(r) = -S_v \left| \frac{C_{++} + C_{--}}{6r^6} \right| = \phi^v(r) \quad (11)$$

where S_v is a lattice sum and the constants C_{++} and C_{--} are the van der Waals coefficients corresponding to the positive-positive and negative-negative ion pairs, respectively.

By solving the secular equation (2) along (q,0,0) direction and subjecting the short and long-range coupling coefficients to the long wavelength limit $\bar{q} \rightarrow 0$, two distinct optical vibration frequencies are obtained as

$$(\mu W_L^2)_{q=0} = R'_0 + \frac{(Z'e)^2}{\nu f_L} \cdot \frac{8\pi}{3} (\xi^2 + 6\xi'^2) \quad (12)$$

$$(\mu W_T^2)_{q=0} = R'_0 - \frac{(Z'e)^2}{vf_T} \cdot \frac{4\pi}{3} \xi^2 \quad (13)$$

where the abbreviations stand for

$$R'_0 = R_0 - e^2 \left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right) \quad Z' = Z_m + d_1 - d_2 \quad (14)$$

$$f_L = 1 + \frac{(\alpha_1 + \alpha_2)}{V} \cdot \frac{8\pi}{3} (Z_m^2 + 6\xi'^2) \quad (15)$$

$$f_T = 1 - \left(\frac{\alpha_1 + \alpha_2}{v} \right) \cdot \frac{4\pi}{3} \xi^2 \quad (16)$$

and $\alpha = \alpha_1 + \alpha_2$

and $v (= 2r_0^3)$ is the volume of unit cell in rock salt structure.

Also α_1, α_2 are the electronic polarizabilities and d_1, d_2 are the distortion polarizabilities of positive and negative ions, respectively.

III. RESULT, DISCUSSION AND CONCLUSION

The Fourteen parameters of our model *VTSM* have been calculated using above expressions (5-16) and presented along with input data in Table 1. These model parameters have been used to compute the phonon dispersion curves of SrO. The calculated phonon dispersion curves of *SrO* have been displayed with experimental data [4] in Figure 1. The agreement between our computed phonon spectra and experimental data is excellent in Table 2. Our model *VTSM* has successfully explained the phonon anomalies even along (q,0,0) and (q,q,q) directions. From figure 1 and Table 2 it is clear that *VTSM*, improves result of *TSM* by 8.3% along *LO(x)*, 5.7% along *TO(x)*, 4.53% along *LA(x)*, 1.3% along *TA(x)*, 4.36% along *LO(L)*, 3.98%, along *TO(L)*, 13.56% along *LA(L)* and 0.33% along *TA(L)* the deviation between theory and experimental due to *TSM* is maximum 13.98% along *LA(L)* while due *VTSM* the deviation is maximum 1.04% along *TA(x)*. However, the predictions of PDC for *SrO* by using *VTSM* may be considered more satisfactory than those from other models [1-4].

The adequacies of *VTSM* have been further tested by studying specific heat variations and two phonon IR/Raman spectra. For this purpose we have computed the specific heats from the phonon spectra and plotted Debye temperature Θ_D the temperature T . It has been presented along with measured data in Figure 2. Our results are in good agreement with measured data [20] and are generally better than by using *BSM* [4]. The small deviation at higher temperature might be mainly due to the anharmonicity involved in the lattice vibrations. As two phonon IR/Raman spectra are sensitive at higher frequency side for this we have employed the critical point analysis [10] to study these properties. A comparison of CDS peaks along with the observed Raman peaks Table 3 and observed IR peaks Table 4 and their assignments from present study has been shown in Figure 3. The basic aim of the study of two phonon IR/Raman scattering spectra is to correlate the neutron and optical experimental data for *SrO*. We have also investigated the anharmonic properties of SrO by using *VTSM* Table (5-6). This includes the predictions of third and fourth order elastic constants and the pressure derivatives of *SOE* and *TOE* constants. The expressions for these elastic constants and pressure derivatives of second order elastic constants derived by us correspond to three-body lattice energy are similar to those derived by Puri, Verma and Garg [23] for *NaCl* structure in the framework of *TSM*. The third order and fourth order elastic constants. Since no experimental values on these properties have been reported so far, we are unable to comment on them but our results will help the experimental workers to analyze their data in future. This study gets strong support from recent publications of our research group [24-43]. To conclude we can say that the present model *SOE VTSM* has successfully explained the phonon properties which include phonon dispersion curves variations of Θ_D with temperature T and combined density of states. Our extensive study on anharmonic properties is to provide physical insight into the nature of binding forces between the constituents of *SrO*. The induction of van der Waals interactions essential in the study of lattice dynamics of ionic crystals.

IV. FIGURE AND TABLES

Table 1: Input data and model parameters for SrO [C_{ij} and B (in 10^{12} dyne / cm^2), ν (in THz), r_0 (in 10^{-8} cm), α_i (in 10^{-24} cm^3), b(in 10^{-12} erg), ρ (in 10^{-8} cm),]

Input Data			Model Parameters	
Properties	Values	Ref.	Parameters	Values
C_{11}	17.33	[15]	b	0.792
C_{12}	4.53	[15]	ρ	0.68
C_{44}	5.60	[15]	$f(r_0)$	-0.348
B	6.87	[15]	$r_0 f'(r_0)$	-0.060942
r_0	2.580	[16]	A_{12}	20.6045
$\nu_{LO}(\Gamma)$	14.40	[4]	B_{12}	12.38929
$\nu_{TO}(\Gamma)$	14.40	[4]	A_{11}	-1.82429
$\nu_{LO}(L)$	13.8	[4]	B_{11}	-4.42713
$\nu_{TO}(L)$	8.28	[4]	A_{22}	5.14596
$\nu_{LA}(L)$	7.08	[4]	B_{22}	-8.87364
$\nu_{TA}(L)$	3.04	[4]	d_1	0.4062674
α_1	1.60	[17]	d_2	0.1868492
α_2	2.095	[17]	Y_1	-4.87299
ϵ_0	8.79	[17]	Y_2	-5.5796537

Table 2. Comparison of frequencies from various sources (X and L points) for SrO

SrO		Expt. [4]	TSM [13]			VTSM (Present study)			% improvement (a-b)
			Value	\pm deviation	% (a)	Value	\pm deviation	% (b)	
X (100)	LO (THz)	9.84	9.01	0.83	8.4	9.85	0.01	0.10	8.3
	TO (THz)	7.41	6.99	0.42	5.6	7.45	0.04	0.53	5.07
	LA (THz)	5.88	5.59	0.29	4.93	5.85	0.03	0.51	4.53
	TA (THz)	3.84	3.75	0.09	2.34	3.80	0.04	1.04	1.30
L (.5.5.5)	LO (THz)	12.84	13.46	0.62	4.82	12.90	0.06	0.46	4.36
	TO (THz)	8.28	8.64	0.36	4.34	8.25	0.03	0.36	3.98
	LA (THz)	7.08	6.89	0.99	13.98	7.05	0.03	0.42	13.56
	TA (THz)	3.04	3.06	0.02	0.65	3.05	0.01	0.32	0.33

Table 3. Comparison of CDS peaks with the observed peaks of second order Raman scattering spectra for SrO

Observed Raman Peaks (cm ⁻¹) [21]	Present Study		
	CDS Peaks (cm ⁻¹)	Assignment	Value (cm ⁻¹)
–	106	–	–
–	141	–	–
–	193	2TA(Δ)	204
350	342	LA + TA(L)	337
–	368	TO + TA(x)	375
–	412	2LA(x)	390
450	465	TO + LA(Δ)	413
–	–	TO + LA(x)	443
–	–	LO + TA(x)	455
–	–	2TO(x)	496
–	–	LO + LA(x)	523
–	543	2TO(L)	550
–	–	LO + TO(x)	576
600	603	LO + TO(x)	596
–	–	2LO(x)	656
–	693	LO + TO(L)	705
750	760	–	–
960	–	–	–

Table 4. Comparison of CDS peaks with the observed peaks of second order IR spectra for SrO

Observed IR Peaks (cm ⁻¹) [22]	Present Study		
	CDS Peaks (cm ⁻¹)	Assignment	Value (cm ⁻¹)
–	106	–	–
–	141	–	–
–	193	2TA(Δ)	204
–	255	–	–
–	342	TO + TA(Δ)	377
387	368	TO + TA(L)	377
–	412	TO + LA(Δ)	413
470	465	2TO(Δ)	470
503	–	LO + LA(L)	507
510	–	LO + TA(Δ)	510
537	543	LO + TA(L)	532
–	603	–	–
–	693	LO + LA(L)	665
813	790	–	–

Table 5. Third and fourth order elastic constants (in units 10¹² dyn/cm²) for SrO

Property	Values	Property	Values
C ₁₁₁	89.4456	C ₁₁₂₂	–4.10844
C ₁₁₂	0.4592	C ₁₂₆₆	0.43587
C ₁₆₆	–0.3157	C ₄₄₄₄	1.57041
C ₁₂₃	0.0650	C ₁₁₂₃	0.39543
C ₁₄₄	0.0722	C ₁₁₄₄	0.32455
C ₄₅₆	0.0848	C ₁₂₄₄	–2.60823
C ₁₁₁₁	132.5991	C ₁₄₅₆	0.20843
C ₁₁₁₂	2.5507	C ₄₄₅₆	0.76095
C ₁₁₆₆	1.0226		

Table 6. Values of pressure derivatives of SOE and TOE constants for SrO

Property	Values
dk' / dP	8.50395
ds' / dP	5.73742
dc'_{44} / dP	8.33855
dc'_{111} / dP	33.68018
dc'_{112} / dP	0.10896
dc'_{166} / dP	1.41868
dc'_{123} / dP	0.81510
dc'_{144} / dP	1.39540
dc'_{456} / dP	1.57249

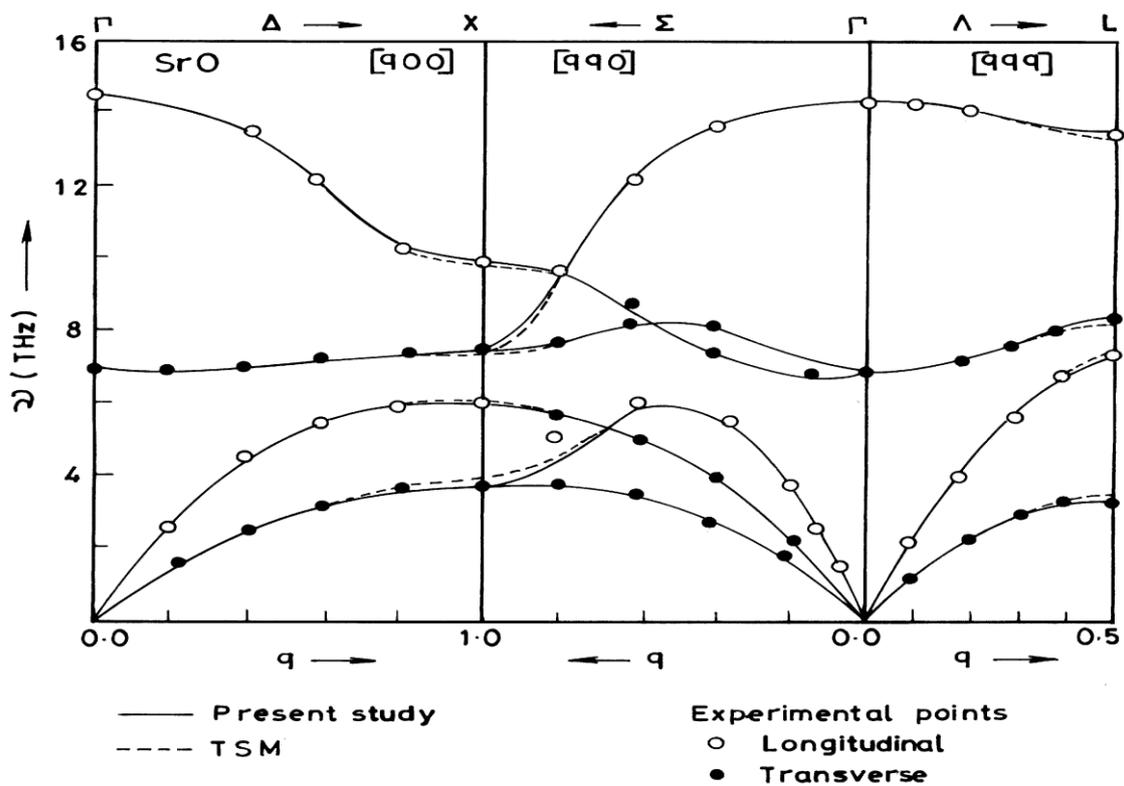


Figure 1: Phonon Dispersion Curve for SrO.

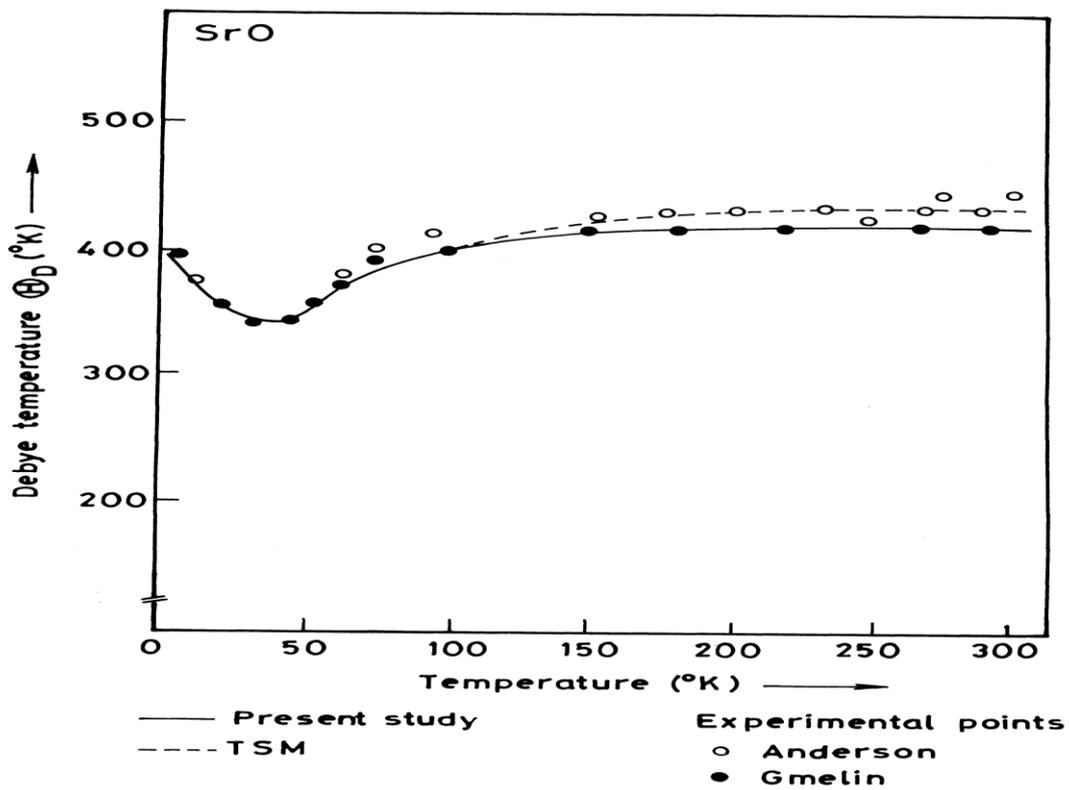


Figure 2: Combined density States (Two phonon) Curve for SrO.

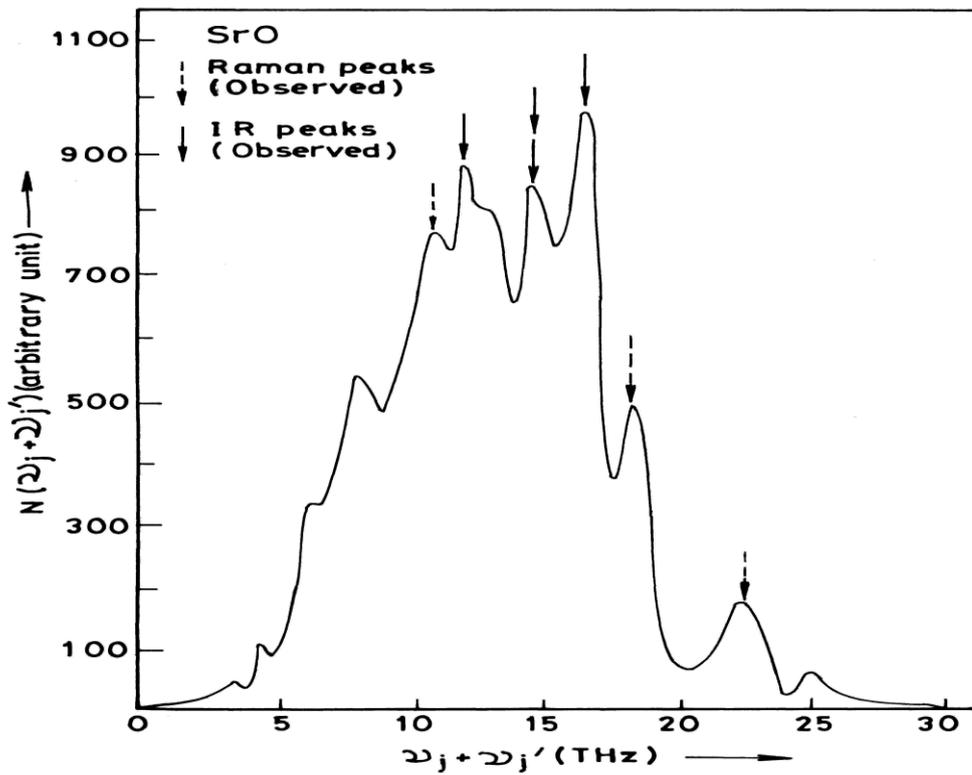


Figure 3: Debye Temperature Variation Curve for SrO.

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