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A Unified Comprative Phonon Dynamical Study of Europium Oxide (EuO) AND Europium Sulphide (EuS)

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Abstract

A systematic unified comparative theoretical analysis of Europium Oxide (EuO) and Europium Sulphide (EuS) has been investigated by a lattice dynamical model which include the effect of three-body interaction (TBI) in the framework of second neighbor three body rigid shell model (SNTRSM) and second neighbor rigid ion model (SNTRIM). These two includes long range Coulomb interactions, three body interactions and short-range second neighbor interactions. The significance of these two approaches thus obtained, have been applied to study the phonon dispersion curves (PDC), variation of Debye temperature with absolute temperature, phonon density of states and anhormonic properties of Europium Oxide (EuO) and Europium Sulphide (EuS) by the supplication of TRSM (three-body force shell model) and TRIM (three-body force rigid ion model). It is concluded that our theoretical results predicted by SNTRSM on phonon dynamics and derivable properties will be very much close to their measured data. The present approach has revealed much better description of the crystal dynamics of the solid than those reported by other models.

Keywords: *Phonon dispersion curves, Rigid shell model, Rigid ion model, Debye temperature*
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INTRODUCTON

The electronic structure of Europium sulfide (EuS) and Europium Oxide (EuO) which is a group of Europium Chalcogenides, solidifies in f.c.c. NaCl structure and are likewise called as uncommon earth europium chalcogenides with incredible intrigue. Dissimilar to other uncommon earth mixes europium chalcogenides by and large, show non-blended valance character. The investigation of cross section dynamical conduct of these chalcogenides is fragmented even today because of deficient exploratory information for phonon scattering bends or curves and a little consideration has been paid to it.

Despite the fact that europium chalcogenides have an enormous application as attractive semiconductors, yet no genuine consideration has paid so for. Just barely any data about the optical frequencies [3-5], versatile elastic properties [2] and magnetic [29, 30] have been introduced. Complete test information on phonon scattering isn't accessible for these mixes aside from EuSe, for which restricted data about phonon recurrence has been accounted for by Silberstein et al. [1]. Zeyher and Kress have applied a phenomenological model (OSM) [14] to talk about the phonon dispersion curves or bends (PDCs) and the

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combined density of states (CDS). Moreover, Osaka et al. [11] have examined the phonon frequencies just for EuSe utilizing Breathing shell model (BSM). For better outcome Mischenko and Kikoin [19] have changed Zayher and Kress overlap shell model (OSM) to foresee the phonon scatterings bends of EuO and EuS. Every one of these analysts changed the dynamical network by consolidating the charge thickness disfigurement impacts. Be that as it may, based on cover accomplishments, their outcomes are for away from progress since none has thought about the many body associations (the primary significant term is three body connections) for these mixes. Because of the unfilled 4f shells, the ionic radii of uncommon earth particle changes and in this manner covering of the chalcogenides particles, likewise changes. The Europium chalcogenides show the deviation from the Cauchy discrepancy C12=C44. The BSM utilized by Onsaka et al. [11] and Sakale et al. [25] of PDC just clarifies the acoustic branches well. Thusly it is clear that OSM and BSM neglect to clarify the optical parts of PDC of these crystals. It has been discovered that three body associations clarify well the optical branches and Cauchy error both at the same time and effectively to practically all the ionic and semiconducting crystals [17]. Also, these mixes showed solid optical phonon oddities all through the Brillouin zone and exceptional acoustic phonon spread along [qqq] bearings. These realities recommend that kinds of many-body collaborations are liable for the flexible and phonon irregularities in these compounds. These have inspired the current creators to the fundamental need of two phenomenological grid dynamical models. The point of this paper is to test the relevance and utility of second neighbor three-body unbending shell model (SNTRSM) and second neighbor three-body inflexible particle model (SNTRIM) for the acceptable portrayal of phonon scattering relations and other phonon properties of these compound mixes .

THEORY

The general formulation of present Lattice Dynamical model is given by

(i) Three-body force rigid shell model (SNTRSM)

(ii) Three-body force rigid ion model (SNTRIM)

The interaction system of present model thus consists of long range Coulomb and three body interactions (TBI) energies. The next term is the form of SR overlap repulsive energy extended to the next nearest neighbor ions in Europium Chalcogenides. As per the interaction system, the present model may positively be the successful attempt for the dynamical description of these materials.

The general formulation of SNTRSM can be derived from the crystal potential whose relevant expression per unit cell is given by

$$\Phi = \Phi^{C} + \Phi^{R} + \Phi^{TBI} \qquad (1)$$

Where the first two terms represent, respectively, long range Coulomb and three body interactions (TBI) energies. The next term is the form of SR overlap repulsive energy extended to the next nearest neighbor ions. where first term Φ^{C} is Coulomb interaction potential which is long-range in nature, second term Φ^{R} is short range overlap repulsion potential operative up to the second neighbors and third term Φ^{TBI} is three body interaction potential. The secular determinant D(q), is the (6x6) dynamical matrix which is given by:

$$D(q) = (R' + Z_m CZ_m) - (T + S_m CY_m)(S + K + Y_m CY_m)^{-1}(T^* + Y_m CZ_m) \quad (2)$$

The Number of adjustable parameters has largely been reduced by considering the short range interaction to act only through the shells. This assumption leads to R=T=S. The expressions derived for elastic constants corresponding to SNTRSM have been obtained as:-

$$\frac{4r_0^4}{e^2} C_{11} = [-5.112Z_m^2 + A_{12} + \frac{1}{2}(A_{11} + A_{22}) + \frac{1}{2}(B_{11} + B_{22}) + 9.3204\xi'^2] \quad (3)$$

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

$$\frac{4r_0^4}{e^2} C_{44} = [2.556Z_m^2 + B_{12} + \frac{1}{4}(A_{11} + A_{22}) + \frac{3}{4}(B_{11} + B_{22})] \quad (5)$$

In View of the equilibrium condition $[(d\,\Phi/dr)_0]$ We obtain.

$$B_{11} + B_{22} + B_{22} = -1.165Z_m^2 \quad (6)$$

Where

$$Z_m^2 = Z^2\left(1 + \frac{12}{Z} f_0\right) \quad \text{and} \quad \xi^{12} = Zr_0 f_0$$

The term f_0 is a function dependent on the overlap integrals of the election wave-funtions and the subscript zero indicates the equilibrium value. By solving the secular equation along [q00] direction and subjection the short and long-range coupling coefficients to the long-wavelength limit $q \to 0$, two distinct optical vibration frequencies are obtained as:

$$(\mu\omega_L^2)_{q=0} = R_0' \frac{(Z'e)^2}{Vf_r} \cdot \frac{8\pi}{3}\left(Z_m^2 + 6\xi'^2\right) \quad (7)$$

$$(\mu\omega_r^2)_{q=0} = R_0' \frac{(Z'e)^2}{Vf_r} \cdot \frac{4\pi}{3} Z_m^2 \quad (8)$$

Since, in these compounds, $\omega_L = \omega_r$ at Γ - point, therefore, Esq. (7) and (8) lead to the expression:

$$\frac{Z_m^2 + 6\xi'^2}{\xi'^2} = -\frac{f_L}{2f_r} \quad (9)$$

Where the abbreviations stand for

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

$$f_L = 1 + \left(\frac{\alpha_1 + \alpha_2}{v}\right).\frac{8\pi}{3}\left(Z_m^2 + 6\xi'^2\right)$$

$$f_r = 1 - \left(\frac{\alpha_1 + \alpha_2}{v}\right).\frac{4\pi}{3}Z_m^2$$

By solving the dynamical matrix along [0.5, 0.5,0.5] directions at L-Point modified expressions for $\omega_{Lo}(L)$, $\omega_{To}(L)$, $\omega_{LA}(L)$, and $\omega_{TA}(L)$, are as follows.

$$m_1\omega_{LA}^2(L) = R_0 + \frac{e^2}{V}(2A_{11} + B_{11} - \frac{e^2 d_1^2}{a_1}$$

$$+\left(\frac{e^2}{V}\right)C_{1L}(Z_m + d_1)^2\left[1 + \left(\frac{\alpha_1}{V}\right)C_{1L}\right]^{-1} \quad (10)$$

$$m_2\omega_{LO}^2(L) = R_0 + \frac{e^2}{V}(2A_{22} + B_{22} - \frac{e^2 d_1^2}{\alpha_1}$$

$$+\left(\frac{e^2}{V}\right)C_{1L}(Z_m + d_2)^2\left[1 + \left(\frac{\alpha_2}{V}\right)C_{1L}\right]^{-1} \quad (11)$$

$$m_2\omega_{TO}^2(L) = R_0 + \frac{e^2}{2V}(2A_{22} + B_{22} - \frac{e^2 d_2^2}{\alpha_2}$$

$$+\left(\frac{e^2}{V}\right)C_{1T}(Z_m + d_2)^2\left[1 + \left(\frac{\alpha_2}{V}\right)C_{1T}\right]^{-1} \quad (12)$$

$$m_1\omega_{TA}^2(L) = R_0 + \left(\frac{e^2}{2V}\right)(A_{11} + 5B_{11} - \frac{e^2 d_1^2}{\alpha_1}$$

$$+\frac{e^2}{V}C_{1T}(Z_m + d_1)^2\left[1 + \left(\frac{\alpha_1}{V}\right)C_{1T}\right]^{-1} \quad (13)$$

where

$$C_{1L}^{'} = -\left[\left(C_{1xx} + 2C_{1xy}\right) + \left(V_{1xx} + 2V_{1xy}\right)Z_m^{-2}Zx_0 f_0^{'}\right]0.5, 0.5, 0.5$$

$$C_{1T}^{'} = -\left[\left(C_{1xx} + C_{1xy}\right) + \left(V_{1xx} + 2V_{1xy}\right)Z_m^{-2}Zr_0 f_0^{'}\right]0.5, 0.5, 0.5$$ where $\left(C_{1xx} + C_{1xy}\right)$ and $\left(V_{1xx} + V_{1xy}\right)$ are Coulomb and three - body coupling coefficients evaluated at L-point. polarizability is negligibly small and the negative ion polarizability of nitride ion is almost zero. Therefore, it has been considered to utilize the second neighbour three-body force rigid ion model (SNTRIM) for further calculations of phonon frequencies.

In an attempt to solve the expressions for SNTRIM, all the Eqs (1-6) will remain the same , only the difference is in the expressions from Eqs. (7-13), which can be written as follows:

$$\left(\mu\omega_L^2\right)_{q=0} = R_0 + \frac{8\pi e^2}{3V}(Z_m^2 + 6\xi'^2) \quad (14)$$

$$\left(\mu\omega_T^2\right)_{q=0} = R_0 - \frac{4\pi e^2}{3V}(Z_m^2) \quad (15)$$

Since, in these compounds, $\omega_L = \omega_T$ at Γ – point, therefore, Eqs (14) and (15) lead to the expression:

$$Z_m^2 = -4Zr_0 f_0' \quad (16)$$

Again, by solving the dynamical matrix along [0.5, 0.5, 0.5] directions at L-point, the modified expressions for $\omega_{Lo}(L)$, $\omega_{To}(L)$, $\omega_{LA}(L)$, and $\omega_{TA}(L)$ are derived as follows:

$$\omega_{LO}(L) = R_0 + \frac{e^2}{v}(2A_{22} + B_{22}) + \frac{e^2}{v}C_{1T}' Z_m^2 \quad (17)$$

$$m_2\omega_{TO}^2(L) = R_0 + \frac{e^2}{v}(A_{22} + 5B_{22}) + \frac{e^2}{v}C_{1T}' Z_m^2 \quad (18)$$

$$m_1\omega_{LA}^2(L) = R_0 + \frac{e^2}{v}(2A_{11} + B_{11}) + \frac{e^2}{v}C_{1L}' Z_m^2 \quad (19)$$

$$m_1\omega_{TA}^2(L) = R_0 + \frac{e^2}{v}(A_{11} + 5B_{11}) + \frac{e^2}{v}C_{1T}' Z_m^2 \quad (20)$$

where R_0 and C_{1T}' have already been defined.

COMPUTATIONS AND RESULTS.

The input data along with their relevant references and calculated model parameters from SMTRSM and SNTRIM for EuO and EuS are given in Table-1 and Table-2. A comparative result on phonon dispersions curves from the two models have been shown in Figure-1and Figure-2. These results have also been compared with the observed data of Kress et al [1].for visual comparison.

Table 1 Input data and model parameters for EuO

[$C_{ij}(in10^{12} dyne\ \mathrm{cm}^{-2})$, v(in THz), $r_0(in10^{-8} cm)$ **and** $\alpha_i(in10^{-24} cm^3)$]

Input Data		**Model Parameters**		
Properties	**Values**	**Parameters**	**TRSM**	**TRIM**
C_{11}	19.2*	Z^2_m	0.7392	0.7238
C_{12}	4.25	$r_0f'0$	-0.0119	-0.0119
C_{44}	5.42	A	7.6432	7.564
$V_{LO}(\Gamma)$	13.05	B	-0.861	-0.8432
$V_{TO}(\Gamma)$	5.460	d_1	0.4145	-
r_0	2.572	d_2	1.1721	-
α_1	2.07	Y_1	-2.0541	-
α_2	2.40	Y_2	-0.8448	-

m

Table 2-Input data and model parameters for EuS

[$C_{ij}(in10^{12}\,dyne\ \mathrm{cm}^{-2})$, v(in THz), $r_0(in10^{-8}\,cm)$ **and** $\alpha_i(in10^{-24}\,cm^3)$]

Input Data		**Model Parameters**		
Properties	**Values**	**Parameters**	**TRSM**	**TRIM**
C_{11}	13.1	Z^2_m	0.6745	0.6522
C_{12}	1.10	$r_0f'_0$	-0.3005	-0.3005
C_{44}	2.73	A	8.5110	8.396
$V_{LO}(\Gamma)$	8.01	B	-0.7858	-0.7598
$V_{TO}(\Gamma)$	5.35	d_1	0.01634	-
r_0	2.984	d_2	1.4081	-
α_1	1.5	Y_1	-0.7943	-
α_2	5.5	Y_2	-2.1497	-

* Value extrapolated from measured PDC

** Reasonable value taken from ionic radii .

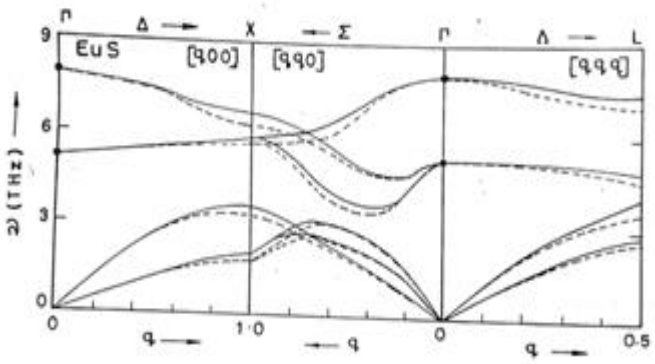

Fig. 1. Phonon dispersion curves for EuS
• Experimental points —— TRSM ----- TRIM

DISCUSSION AND CONCLUSION

From figure 1 and 2, it is clear that the results reported from SNTRSM for EuO and EuS. EuS are comparatively more close to ensured data on PDCs. There are certain features in PDC of EuS which deserve special mention. The three body interactions have influenced both LO and TO branches much more than acoustic braches (LA and TA). Another striking feature of the present study is noteworthy from the excellent reproduction of optical and acoustic branches.

The model parameters of TRSM and TRIM have been used to calculate the phonon spectra for allowed 48 non-equivalent wave vectors in first Brillouin zone. The frequency along with symmetry directions have been plotted against the wave vectors to obtain the phonon dispersion curves (PDCs) from both the models. These curves are compared with each other and with inelastic neutron scattering technique.

Since neutron scattering provide us only a very little data for symmetry direction, we have studied the specific heat for complete description of frequencies. For this purpose the specific heat has been computed at different temperature using Blackmann's technique [35] and corresponding Debye temperature have been plotted against absolute temperature (T).

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It may be concluded that SNTRSM provides agreement which is certainly better than those fitted by experimental researchers and SNTRIM, are very much close to the experimental values. Although, qualitatively the agreement achieved from our present model SNTRSM is comparatively better than some of the model values. In addition, some other researchers [18-24] of the field have also tried their best to explain PDCs and other properties of europium chalcogenides but only with moderate success.

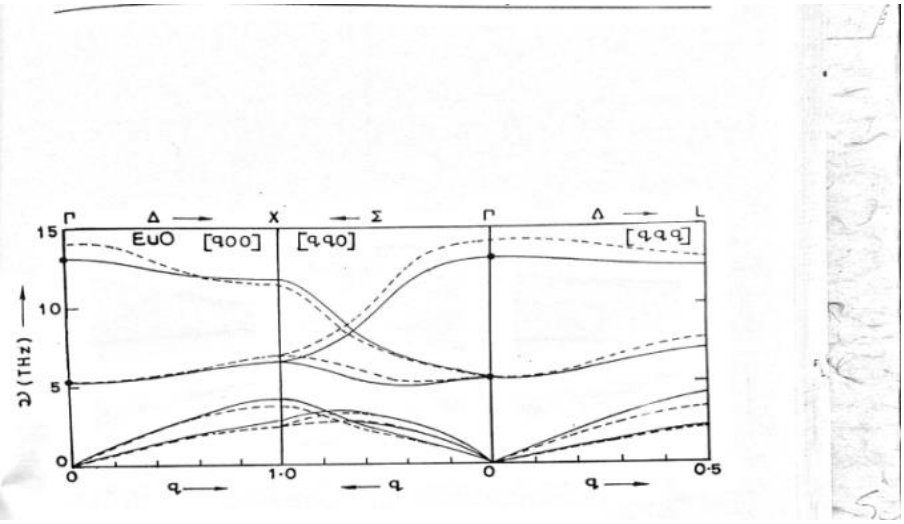

Figure-2 Phonon dispersion curves of EuO.
Experimental points -------TRSM
--------TRIM

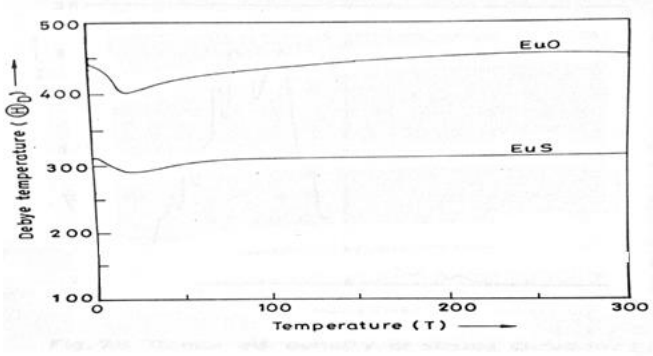

Figure-3 Debye temperature variations of EuO and EuS

Furthermore, in order to increase the merit of this work, we have tested the adequacy of our model by calculating [33] two phonon Raman/IR spectra and variation of Debye temperatures shown in figure-3. In order to interpret them the critical point analysis has been used following the method prescribed by Burstein et al [36].

It may be concluded that the inclusion of the effect of short range overlap repulsive interaction upto second neighbours in the framework of TRIM and TRSM is important in EuO and EuS. These are probably the first reports of its kind and this will help the other workers to analyze their data in future.

Furthermore, It is expected that slight discrepancies still occurring between theory and experiment may be further improved by including the effect of free carrier screening (FCS), Van der Waals interactions (if data are available in future) and by including anharmonicity of vibrations in the present model (SNTRSM).

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