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Phonon dispersion curves of TiN

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A lattice dynamical model which includes the effect of three-body interactions (TBI) in the framework of second neighbour rigid shell model (SNTRSM) and second neighbour rigid ion model (SNTRIM) has been developed. The models, thus obtained, have been applied to study the phonon dispersion curves (PDCs) of TiN along the principal symmetry directions. It is found that SNTRSM explains well the phonon anomalies in the experimental PDCs of TiN as compared to SNTRIM and other models.

Keywords: Phonon dispersion, TiN, Rigid shell model, Rigid ion model
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1 Introduction

Recently, transition metal carbides (TMC) and transition metal nitrides (TMN), of the group **iv**b, **v**b and **vi**b (transition metals), form a class of materials with an unusual combination of physical properties. They combine extremely high melting point and hardness with metallic conductivity. Some of them are superconductors and show anomalies (NbC and TaC) in the phonon dispersion curves (PDCs) whereas no anomalies were found in non-superconducting compounds (ZrC, HfC). It was an open question for nitrides whether they show anomalies in the PDCs like carbides. Kress *et al.*[1] observed the soft mode behaviour in superconducting TiN by inelastic neutron scattering experiment and their measurements gave conclusive evidence for the existence of pronounced phonon anomalies in its PDCs (Fig. 1). There are pronounced minima in the LA branches in the PDCs of TiN, specially along [qoo]at q=0 .65 and [qqo] at q=0.55 in the Δ and Σ directions, respectively and at the L-point. The TA branch at the L-point appears only slightly depressed. Kress *et al.*[1] have used the double shell model (DOSM) for explaining their measured phonon anomalies in PDCs. This model could describe their result very well by fitting the parameters of DOSM but some of the values of their parameters are physically unrealistic. Hence, DOSM failed to explain the physical properties exhibited by TiN. The polarizability of negative ion is negligibly small, and that of positive ion only comes to play role in their DOSM. Due to the absence of ionic polarizabilities and less number of free carriers present in TMN, the effect of free carriers screening has been neglected by us in our earlier model[2]. The aim of the present paper is to test the applicability of second neighbour three-body force rigid shell model (SNTRSM) and second neighbour three-body force rigid ion model (SNTRIM) in order to describe the phonon dispersion relations of TiN.

2 Theory of Models

Essential formalism of the present lattice dynamical models is given as:

(i) Three-body force rigid shell model [SNTRSM]; (ii) Three-body force rigid ion model [SNTRIM]

The interaction system of the present models thus consists of the long-range Coulomb and three-body interactions and the short range overlap repulsiv interaction operative upto the second (next nearest) neighbour ion in transition metal nitrides (TMN). Looking into the adequacy of these interaction systems, the present models may hopefully be regarded as a successful approach for the dynamical description of these compounds. The general formalism of SNTRSM can be derived from the crystal potential whose relevant expression per unit cell is given by:

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

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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 upto the second neighbours and third term Φ^{TBI} is three-body interaction potential. The secular determinant *D(q),* is the (6×6) dynamical matrix which is given by:

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

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:

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

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

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

In view of the equilibrium condition $[(d\Phi/dr)_0 = 0]$ we obtain

$$B_{11} + B_{22} + B_{12} = -1.165Z_m^{\,2} \quad \ldots(6)$$

where

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

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

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

$$\left(\mu\omega_T^{\,2}\right)_{q=0} = R_0' - \frac{(Z'e)^2}{Vf_T}.\frac{4\pi}{3}\ Z_m^{\,2} \quad \ldots(8)$$

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

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

where the abbreviations stand for

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

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

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

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:

$$m_1\omega_{LA}^2(L) = R_0 + \frac{e^2}{V}(2A_{11} + B_{11}) - \frac{e^2 d_1^2}{\alpha_1} + \left(\frac{e^2}{V}\right)C_{1L}'(Z_m + d_1)^2\left[1 + \left(\frac{\alpha_1}{V}\right)C_{1L}'\right]^{-1} \quad \ldots(10)$$

$$m_2\omega_{LO}^2(L) = R_0 + \frac{e^2}{V}(2A_{22} + B_{22}) - \frac{e^2 d_2^2}{\alpha_2} + \frac{e^2}{V}C_{1L}'(Z_m - d_2)^2\left[1 + \left(\frac{\alpha_2}{V}\right)C_{1L}'\right]^{-1} \quad \ldots(11)$$

$$m_2\omega_{TO}^2(L) = R_0 + \left(\frac{e^2}{2V}\right)(A_{22} + 5B_{22}) - \frac{e^2 d_2^2}{\alpha_2} + \frac{e^2}{V}C_{1T}'(Z_m - d_2)^2\left[1 + \left(\frac{\alpha_2}{V}\right)C_{1T}'\right]^{-1} \quad \ldots(12)$$

$$m_1\omega_{TA}^2(L) = R_0 + \left(\frac{e^2}{2V}\right)(A_{11}+5B_{11}) - \frac{e^2 d_1^2}{\alpha_1} + \frac{e^2}{V} C_{1T}^{'}(Z_m + d_1)^2 \left[1 + \left(\frac{\alpha_1}{V}\right) C_{1T}^{'}\right]^{-1} \quad \ldots(13)$$

where

$$C_{1L}' = -\left[(C_{1xx} + 2C_{1xy}) + (V_{1xx} + 2V_{1xy})\, Z_m^{-2}\, Zr_0\, f_0'\right]_{0.5,0.5,0.5}$$

and

$$C_{1T}' = -\left[(C_{1xx} - C_{1xy}) + (V_{1xx} - V_{1xy})\, Z_m^{-2}\, Zr_0\, f_0'\right]_{0.5,0.5,0.5}$$

where (C_{1xx}, C_{1xy}) and (V_{1xx}, V_{1xy}) are Coulomb and three-body coupling coefficients evaluated at L-point.

We know that for TMN, the positive ion 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:

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

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

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

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

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:

$$m_2\omega_{LO}^2(L) = R_0 + \frac{e^2}{v}(2A_{22}+B_{22}) + \frac{e^2}{v} C_{1L}'\, Z_m^2 \quad \ldots(17)$$

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

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

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

where R_0, C'_{1L} and C'_{1T} have already been defined.

3 Computations and Results

The input data alongwith their relevant references and calculated model parameters from SMTRSM and SNTRIM for TiN are given in Table 1. A comparative results on phonon dispersions curves from the two models have been shown in Figure 1. 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 TiN [C_{ij} (in 10^{12} dyne cm^{-2}), ν (in THz), r_0 (in 10^{-8} cm) and α_i (in 10^{-24} cm^3)]

Input data Properties	Values	Model parameters		
		Parameters	SNTRSM	SNTRIM
C_{11}	6.25[a]	Z_m^2	0.9148	0.1144
C_{12}	1.65[a]	$r_0 f'(r_0)$	0.02	0.02
C_{44}	1.63[a]	A_{12}	9.5398	2.6499
$\nu_{LO}(\Gamma)=\nu_{TO}(\Gamma)$	14.76[b]	B_{12}	–1.0657	–0.0969
$\nu_{LO}(L)$	18.73*	A_{11}	–13.5183	19.3796
$\nu_{TO}(L)$	16.98*	B_{11}	–3.8587	–0.9646
$\nu_{LA}(L)$	9.04[b]	A_{22}	–7.1417	0.6942
$\nu_{TA}(L)$	5.87[b]	B_{22}	–1.2611	0.4204
α_1	0.19[c]	d_1	0.4354	–
r_0	2.06**	Y_1	–0.7530	–

a – [3] *b* – [1] *c* – [4]
*Values extrapolated from measured PDC
**Reasonable value taken from ionic radii

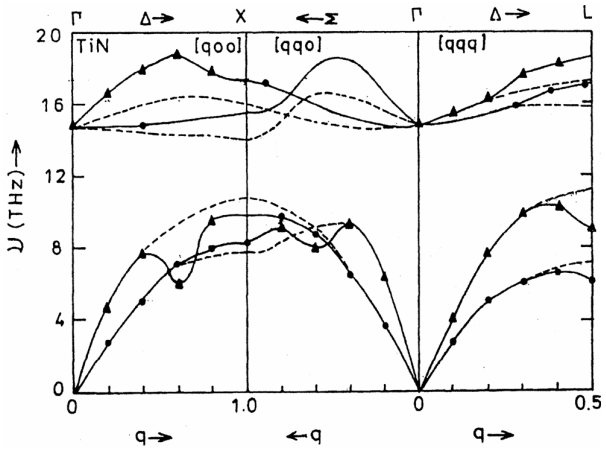

Fig. 1 — Phonon dispersion curves of TiN

4 Discussion and Conclusion

From Figure 1, it is clear that the results reported from SNTRSM for TiN are comparatively more close to the measured data on PDCs. These results are similar[2] to the TMC but there are certain features in PDC of TiN which deserve special mention. The three body interactions have influenced both LO and TO branches much more than accoustic braches (LA and TA). Another striking feature of the present study is noteworthy from the excellent reproduction of optical and acoustic branches.

A qualitative comparison amongst frequencies of experimental PDC and those reported from present models[5] has been made at X-and *L* points in the Table 2.

It may be concluded from Table 2 that SNTRSM provides agreement which is certainly better than those fitted by DOSM (experimental researchers) and SNTRIM. The maximum deviation is 2-3%. The frequencies at *X* and *L* points reported from SNTRSM are very much close to the experimental values (Table 2). Although, qualitatively the agreement achieved from our present model SNTRSM is comparatively better in the sense that some of the DOSM fitted parameters of Kress *et al.*[1] have attained unrealistic values. In addition, some other researchers[5-9] of the field have also tried their best to explain PDCs and other properties of transition metal nitrides but only with moderate success. Furthermore, in order to increase the merit of this work, we have tested the adequacy of our model by calculating[10] two phonon Raman/IR spectra and variation of Debye temperatures. Combined density of states curves have also been studied and explained with critical point analysis. They are in good agreement with available experimental data.

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 TiN. The present approach has revealed much better description of the crystal dynamics of the solid under consideration than those reported[1] by DOSM. Furthermore, the inherent shortcomings of the present models are most likely the same as the demerits of models RIM and RSM. 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 anharmoncity of vibrations in the present model (SNTRSM).

Table 2 — Comparison of frequencies from various sources (X and L points) for TiN

Source	Frequencies (THz)			
	LO(*X*)	*TO*(*X*)	*LA*(*X*)	*TA*(*X*)
Experimental	–	–	–	8.25
SNTRSM	17.30	15.55	9.70	8.25
SNTRIM	16.00	14.00	10.80	7.80
	LO(*L*)	*TO*(*L*)	*LA*(*L*)	*TA*(*L*)
Experimental	–	–	9.04	5.87
SNTRSM	18.7	17.00	9.00	6.00
SNTRIM	17.30	15.80	11.20	7.20

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