PRAMANA
— journal of
physics

Vol. 64, No. 2
February 2005
pp. 299–304

Lattice vibrational properties of transition metal carbides (TiC, ZrC and HfC)

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MS received 23 September 2003; revised 24 August 2004; accepted 27 August 2004

Abstract. Lattice vibrational properties of transition metal carbides (TiC, ZrC and HfC) have been presented by including the effects of free-carrier doping and three-body interactions in the rigid shell model. The short-range overlap repulsion is operative up to the second neighbour ions. An excellent agreement has been obtained between theory and experiment for their phonon dispersion curves and Debye temperature variations. It is concluded that the contributions of free-carrier doping and three-body interactions are essential for the description of the lattice dynamics of these carbides.

Keywords. Lattice vibrational; phonon dispersion curves; free-carrier three-body shell model; transition metal carbides.

PACS Nos 63.20.Dj; 63.10.+a; 62.50

1. Introduction

The study of lattice dynamics of transition metal carbides (TMC) has been the object of considerable and continuing interest in solid state physics. Transition metal carbides (TiC, ZrC, HfC, NbC and TaC) are complex crystals with significant ionic, covalent and metallic characters. Some of them (TaC and NbC) are superconductors with high transition temperature ($T_c \approx 10$ K) and their superconducting properties are closely related to the formal valence of the metal and non-metal while TiC, HfC and ZrC, having eight valence electrons, are non-superconductors with low T_c (< 0.05 K).

Because of their unique physical properties and degeneracy in optical vibration frequencies at the zone center (Γ-point), these carbides have always contributed fascinating and challenging fields for both theoretical and experimental workers. This fact is self-evident from the development of numerous phenomenological models for predicting the available experimental data on phonon dispersion, specific heats, harmonic and anharmonic elastic constants and optic constants. The detail of the progression has been traced in review articles by Toth [1], Bilz and Kress

[2], Singh and Gupta [3] and research papers [4–13]. The degeneracy of the optical vibration frequencies of the zone center is common to all the transition metal carbides. The experimental information about these ionic semiconductors is provided from the phonon dispersion data [14–17]. A survey of the literatures on the application of various models discussed in [18–22] to binary ionic solids has yielded almost satisfactory description of their lattice dynamical, elastic and optical properties. However, few of these models have been employed for the prediction of the most reliable phonon data measured accurately by the inelastic neutron scattering technique for these compounds.

The primary aim of the present study is to include free-carrier doping (FCD) [23] and three-body interactions (TBI) in the framework of both ions polarizable RSM.

2. Theory of FTSM

The dynamical matrix for the present model is defined as

$$\underline{D}(q) = (\underline{R} + \underline{Z}_m \underline{C'} \underline{Z}_m) - (\underline{T} + \underline{Z}_m \underline{C'} \underline{Y}_m) \times (\underline{S} + \underline{K} + \underline{Y}_m \underline{C'} \underline{Y}_m)^{-1} (\underline{T}^T + \underline{Y}_m \underline{C'} \underline{Z}_m), \tag{1}$$

where $\underline{K}$ is a diagonal matrix representing the force constant between the core and the shell of the ions. The original core and shell charges (X, Y) of RSM have been modified to (X_m, Y_m) and given by

$$Z_m = \pm Z[1 + (12/Z) f_0]^{1/2} = X_m + Y_m = XZ_m + YZ_m, \tag{2}$$

where $f[= f(r)_0]$ is the three-body force parameter which depends on the equilibrium interionic separation (r_0) and overlap integrals [21]. Further, the expressions for the second-order elastic constants (C_{11}, C_{12}, C_{44}) are as follows:

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

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

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

where (A_{12}, B_{12}) and $(A_{11}, B_{11}, A_{22}, B_{22})$ are the short-range parameters for the nearest and the next neighbours, respectively. The zone-center vibration frequencies $(\nu_{\mathrm{L}}, \nu_{\mathrm{T}})$ can be expressed as

$$(4\pi^2 \mu \nu_{\mathrm{L}}^2)_{q=0} = R_0' + \frac{8\pi}{3} \frac{(Z'e)^2}{V f_{\mathrm{L}}} (Z_m^2 + 6\xi'^2 + E_0), \tag{6}$$

Table 1. Model parameters for TiC, ZrC and HfC.

	TiC	ZrC	HfC
$f_0(r_0)$	0.0250	0.0300	0.0070
$r_0 f_0'(r_0)$	−0.3240	−0.3400	−0.2690
A_{12}	20.3410	21.9240	21.6550
B_{12}	−0.0820	−1.5170	−1.6730
A_{11}	10.7190	16.0360	19.4580
B_{11}	−1.2170	−0.1620	−2.1020
A_{22}	7.8150	10.1610	3.0920
B_{22}	−0.1510	0.0930	2.5190
d_1	0.2415	0.3007	0.4276
d_2	0.0123	0.0123	0.0123
Y_1	−0.6098	−0.6347	−0.6816
Y_2	−0.6469	−0.4194	−0.4558

$$(4\pi^2\mu\nu_{\mathrm{T}}^2)_{q=0} = R_0' - \frac{4\pi}{3}\frac{(Z'e)^2}{Vf_{\mathrm{T}}}(Z_m^2 + E_0). \tag{7}$$

Since, in these carbides $\nu_{\mathrm{L}} = \nu_{\mathrm{T}}$ at Γ-point, eqs (6) and (7) lead to the expression

$$\frac{Z_m^2 + 6\xi'^2 + E_0}{Z_m^2 + E_0} = -\frac{f_{\mathrm{L}}}{2f_{\mathrm{T}}}, \tag{8}$$

where the abbreviations stand for

$$Z' = Z_m + d_1 - d_2, \tag{9}$$

$$R_0' = R_0 - e^2\left(\frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2}\right), \tag{10}$$

$$R_0 = \frac{(Ze)^2}{V}[A_{12} + 2B_{12}], \tag{11}$$

$$f_{\mathrm{L}} = 1 + \left(\frac{\alpha_1 + \alpha_2}{V}\right)\frac{8\pi}{3}(Z_m^2 + 6\xi'^2 + E_0), \tag{12}$$

$$f_{\mathrm{T}} = 1 - \left(\frac{\alpha_1 + \alpha_2}{V}\right)\frac{4\pi}{3}(Z_m^2 + E_0), \tag{13}$$

and $\alpha = \alpha_1 + \alpha_2$. E_0 is the term corresponding to FCD.

3. Results and discussion

Our model FTSM, described in the preceding section, has been applied to study the dynamical behaviour of transition metal carbides (TiC, ZrC and HfC). The model

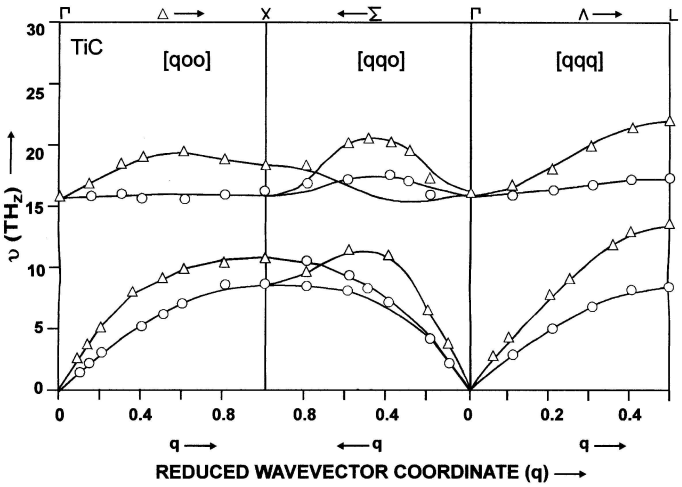

Figure 1. Phonon dispersion curves for TiC. Experimental points [5] (△ Longitudinal, ○ transverse).

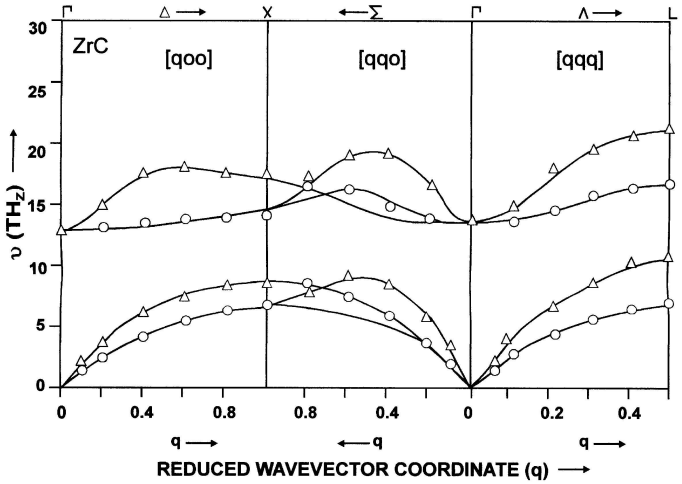

Figure 2. Phonon dispersion curves for ZrC. Experimental points [7] (△ Longitudinal, ○ transverse).

parameters have been determined from the knowledge of experimental values of the equilibrium interatomic separation (r_0), the elastic constants (C_{11}, C_{12}, C_{44}), the zone-centre frequencies $\nu_{\mathrm{LO}}(= \nu_{\mathrm{TO}})$, ν_{LO} (L) and ν_{TA} (L). The input data have been presented elsewhere [18] and the model parameters are given in table 1 for TiC, ZrC and HfC.

The phonon dispersion curves have been obtained by plotting these vibration frequencies against the wave vector (q) and displayed in figures 1–3 for TiC, ZrC and HfC, respectively. Figures 1–3 show that the phonon dispersion curves (PDC) for all these carbides are almost similar but there are certain features, which deserve

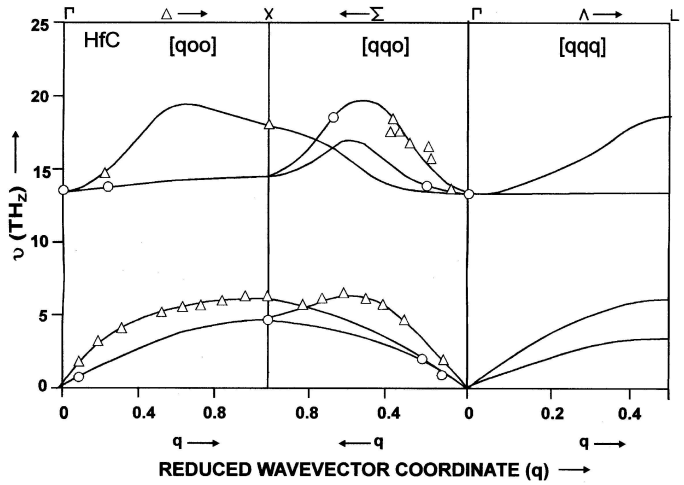

Figure 3. Phonon dispersion curves for HfC. Experimental points [8] (△ Longitudinal, ○ transverse).

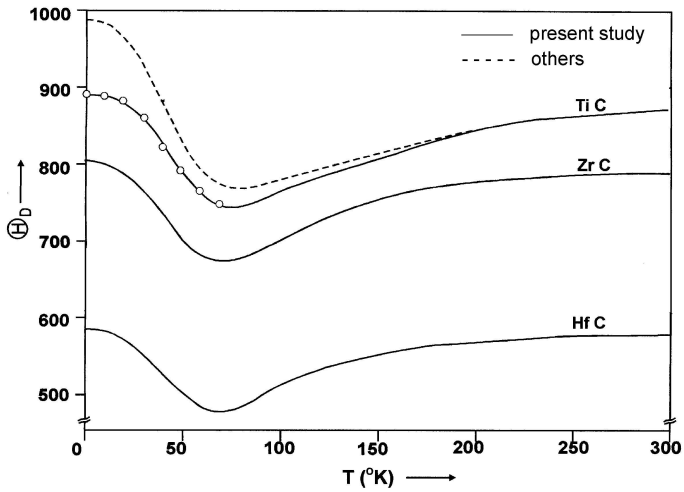

Figure 4. Debye temperatures variation for TiC, ZrC and HfC. Experimental points ○ [5].

special mention. Three-body interactions have influenced LO and TO branches much more in these crystals. A qualitative interpretation of the general features of PDC is also obvious from the present model when it predicts the gap between the acoustic and optical branches similar to forbidden gap between the valence and the conduction band. The variations of Debye temperature with temperature (T) are shown in figure 4 for TiC, ZrC and HfC. The calculated (Θ_D–T) curves for crystals are in good agreement with the experimental results [5]. In ZrC and HfC the measured data on Debye temperature variation are not available as yet.

In view of the overall achievements described above, it is concluded that the modifications introduced by the FCD and TBI in the framework of RSM is important in transition metal carbides. In fact, the present model FTSM has revealed much better descriptions of the dynamical properties of these carbides.

Acknowledgements

The authors are grateful to the computational assistance provided by the computer centre, Banaras Hindu University, Varanasi.

References

[1] L E Toth, *Transition metal carbides and nitrides* (Academic Press, New York, 1971)
[2] H Bilz and W Kress, *Springer series in solid state sciences* **10**, 1 (1979)
[3] R K Singh and H N Gupta, *Solid State Commun.* **16**, 197 (1975)
[4] R K Singh, *Phys. Reports* (Netherlands) **85**, 259 (1982)
[5] L Pinschovius, W Reichardt and B Scheeres, *J. Phys.* **C11**, 1557 (1978)
[6] H G Smith, in *Proceedings of the International Conference on Phonons* (Rennes, France, 1971) edited by M Nusimovice (Flammarion Paris, 1971)
[7] H G Smith, N Wakabayashi, R M Nicklow and S Mihalovich, in *Proc. 13th Int. Conf. on Low Temperature Physics*, USA (1972)
[8] H G Smith and W Glasser, *Phys. Rev. Lett.* **25**, 1611 (1970); **29**, 353 (1972)
[9] W Weber, *Phys. Rev.* **B8**, 5082 (1973)
[10] W Weber, *Phys. Rev.* **B8**, 5093 (1973)
[11] W Weber, H Bilz and U Schroder, *Phys. Rev. Lett.* **28**, 600 (1972)
[12] M P Verma and B R K Gupta, *Phys. Rev.* **B12**, 1314 (1975)
[13] P T Jochym and K Parlinski, *Euro. Phys. J.* (France) **B15**, 265 (2000)
[14] W A Mackie, P Carieson, J Fillon and C H Himrich, *J. Appl. Phys.* (USA) **169**, 7236 (1991)
[15] A Fernandez Guillermet, *J. Alloys Comp.* **217**, 69 (1995)
[16] S Eroglu and B Gallois, *J. Mat. Sci.* **30**, 1754 (1995)
[17] K Albersten and H J Schaller, *Z. Metallk. d.* **86**, 319 (1995)
[18] Ajay Kumar Singh, Ph.D. Thesis (VBS University, Jaunpur, 2001)
[19] E W Kellermann, *Philos. Trans. R. Soc. London* **A230**, 513 (1940)
[20] M P Verma and R K Singh, *Phys. Status Solidi* **33**, 769 (1969); **36**, 335 (1969); **38**, 851 (1970)
[21] P O Lowdin, *Ark. Mat. Astr. Fys.* **A35**, 30 (1947)
[22] A D B Woods, W Cochran and B N Brockhouse, *Phys. Rev.* **119**, 980 (1960)
[23] R A Cowley and G Dolling, *Phys. Rev. Lett.* **14**, 548 (1965)