PHYSICAL REVIEW B VOLUME 12, NUMBER 4 15 AUGUST 1975

Three-body-force shell-model study of phonon dispersion in the transition-metal carbides TaC and HfC

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(Received 21 May 1974)

Phonon dispersion curves of two transition-metal carbides TaC and HfC have been derived from the three-body-force shell model (TSM). To account for the absence of the Lyddane-Sachs-Teller splitting between the long-wave optic-mode frequencies the model has to be so set as to give a zero value to the Lundqvist effective charge. The TSM results are found to agree well with the experimental curves of Smith and Glaser and are in this regard much better than the pseudopotential calculations of Mostoller and almost as good as the double-shell-model and the simple-screened-shell-model results of Weber for TaC and HfC, respectively.

I. INTRODUCTION

Since the publication of the neutron spectroscopic measurements of the phonon frequencies of the transition-metal carbides by Smith and Glaser[1,2] a number of theoretical studies[3-6] have been reported which interpret the dispersion curves either on the basis of a modified shell model or through a pseudopotential formulation. The transition-metal carbides have certain points of similarity with ionic and covalent solids, as also with metals. Thus these solids generally crystallize in the NaCl structure, are hard, and have very high melting points, similar to the homopolar crystals. They also have large electrical conductivities and change over to superconducting states at transition temperatures T_c, which in many cases are much higher than in the case of simple-metal superconductors. It is therefore no wonder that both the shell-model and pseudopotential theories are able to explain the dispersion relations in these solids with some success.

The shell model (SM) with its various modifications has successfully explained the dispersion relations in the ionic and covalent crystals,[7-12] and the best description of the dynamical behavior of ionic lattices is obtained from the breathing shell model (BSM)[13] and the three-body-force shell model (TSM),[14] which are to a large extent equivalent to each other.[15,16] However, as shown by Sinha,[17] there is a close connection between the shell model and the pseudopotential theory for the lattice dynamics of metals, so that the shell model can with suitable choice of parameters describe the dynamical behavior of metallic lattices also. A suitably modified shell model can therefore be expected to present a satisfactory explanation of the dispersion relations in the transition-metal carbides. It may be pointed out here that different modified versions of the shell model applied to these crystals (Bilz,[3] Weber,[4] Weber *et al.*[5]) present much better agreements with the experimental dispersion curves than the one obtained by the pseudopotential calculations of Mostoller.[6]

An interesting feature of the dispersion curves of high-T_c solids like TaC (Refs. 1, 18) and Nb (Ref. 19) is the existence of anomalous wiggles in certain branches. This anomaly is supposed to be caused by some very-long-range ion-ion interactions.[19] As suggested by Ganguly and Wood,[20] this long-range interaction may be obtained by considering the electron-phonon interaction self-consistently: in other words, by including the ω- and $\vec{q}$-dependent dielectric response function $\epsilon(\vec{q}, \omega)$. This suggestion has led Weber *et al.*[4,5] to use in their analysis a short-range screened ion-electron-ion interaction term. They have thus developed a simple screened shell model (SSM) for low-T_c solids and a double shell model (DSM) with the screening term for high-T_c solids. These models give a satisfactory explanation of the phonon dispersion curves. The anomalous wiggles in high-T_c solids have been explained as arising due to a resonance effect. The resonance condition leads to the conclusion that the charge density represented by the new electronic degree of freedom is weakly bound at the metal ions and is in an unstable position with respect to the displacements of neighboring charge densities.

As against this, the TSM is obtained by injecting a long-range three-body interaction into the simple shell model by Woods *et al.*[21] Classically, the three-body forces arise due to a charge transfer between neighboring ions and the transferred charge varies with the relative displacements of nearest neighbors.[15] In this sense the physical content of the TSM is nearly the same as that of the DSM. The TSM is therefore expected to explain the dispersion relations in the transition-metal carbides, particularly those with high T_c, sufficiently well. Further, the TSM study of these solids will definitely reveal whether or not the long-range ion-ion interaction responsible for the anomalous wiggles in the dispersion curves can be identified with the long-range three-body interaction in ionic solids derived by Löwdin[22] and Lundqvist.[23]

With this object in view we have applied the TSM with a suitable modification to all the transition-metal carbides. In this first communication we are reporting results on TaC and HfC. The latter has a low value of T_c and its phonon dispersion curves do not exhibit the anomalies observed in the case of TaC. The TSM results on both TaC and HfC compare very well with the results of Weber and reproduce all the features of the experimental phonon dispersion curves to a very good approximation.

Quantum-mechanically, the TSM is based on the Heitler-London approximation, while the SSM and DSM use a free-electron-like screening of ion-ion interaction. We can therefore conclude that the behavior of electrons in transition-metal carbides is described equally well by both the Heitler-London approximation and the free-electron approximation. In Sec. II we discuss the applicability of the TSM equations to the metal carbides under consideration, and in Sec. III the results of our calculations. A short discussion follows in Sec. IV.

II. TSM EQUATIONS FOR TRANSITION-METAL CARBIDES

The TSM equations have recently been corrected by Verma and Agarwal[24] by choosing expressions for the core and shell charges and hence of the electronic and distortion polarizabilities consistent with the dynamical equations of the model. The authors have also presented in this work a classical derivation of the Lundqvist potential based on the idea of charge transfer due to overlap of outer electron shells of neighboring ions. Since the second neighbors in the NaCl structure are of the same kind there cannot be a charge transfer between them. This implies that the second-neighbor overlap will not modify the three-body interaction term in the lattice potential. In other words, the second-neighbor overlap potential can be included in the TSM without modifying the three-body coupling coefficients. Since the carbon ion in the transition-metal carbides is relatively small, the metal ions are expected to overlap substantially and the second-neighbor short-range interaction between these ions may not be negligible. Inclusion of this interaction modifies the basic equations determining the model parameters to

$$C_{11}=\frac{e^2}{4a_0^4}\left[-5.112Z[Z+12f(a)]+A+\frac{A'+B'}{2}+9.3204Z\left(a\frac{df(a)}{da}\right)\right], \tag{1}$$

$$C_{12}=\frac{e^2}{4a_0^4}\left[0.226Z[Z+12f(a)]-B+\frac{A'-5B'}{4}+9.3204Z\left(a\frac{df(a)}{da}\right)\right], \tag{2}$$

$$C_{44}=\frac{e^2}{4a_0^4}\left(2.556Z[Z+12f(a)]+B+\frac{A'+3B'}{4}\right), \tag{3}$$

where A' and B' are related to the short-range potential ${}^R\phi_2$ coupling the nearest-neighbor metal-metal ions through

$$\frac{e^2\sqrt{2}A'}{4(a\sqrt{2})^3}=\left(\frac{d^2({}^R\phi_2)}{dr^2}\right)_{r=a\sqrt{2}}, \tag{4a}$$

$$\frac{e^2\sqrt{2}B'}{4(a\sqrt{2})^3}=\left(\frac{1}{r}\frac{d({}^R\phi_2)}{dr}\right)_{r=a\sqrt{2}}, \tag{4b}$$

and the other parameters have the same meanings as in the corrected TSM equations of Verma and Agarwal.[24] The equilibrium condition now reads

$$B+B'=\tfrac{1}{3}2\alpha_M Z[Z+12f(a)] \tag{5}$$

and the long-wave optical vibration frequencies are given by

$$(\mu\omega_L^2)_{q\to 0}=R_0'+\frac{(Z'e)^2}{vf_L}\times\frac{8\pi}{3}Z\left(Z+12f(a)+6a\frac{df(a)}{da}\right), \tag{6}$$

$$(\mu\omega_T^2)_{q\to 0}=R_0'-\frac{(Z'e)^2}{vf_T}\times\frac{4\pi}{3}Z[Z+12f(a)], \tag{7}$$

where

$$R_0'=R_0-e^2\left(\frac{d_1^2}{\alpha_1}+\frac{d_2^2}{\alpha_2}\right), \tag{8}$$

$$R_0=\frac{e^2}{v}(A+2B), \tag{9}$$

$$d_\kappa=\frac{e^2Y_\kappa^2 Z[Z+12f(a)]}{k_\kappa+R_0}, \qquad \kappa=1,\ 2 \tag{10}$$

$$Z'=1-\frac{d_2-d_1}{\{Z[Z+12f(a)]\}^{1/2}}, \tag{11}$$

$$d_\kappa=-\frac{R_0Y_\kappa\{Z[Z+12f(a)]\}^{1/2}}{k_\kappa+R_0}, \qquad \kappa=1,\ 2 \tag{12}$$

$$f_L=1+\frac{8\pi\alpha Z\{Z+12f(a)+6a[df(a)/da]\}}{3vZ[Z+12f(a)]}, \tag{13}$$

$$f_T=1-\frac{4\pi\alpha}{3v}. \tag{14}$$

k_κ are the isotropic force constants coupling the core and shell of the κth ion and $eY_\kappa\{Z[Z+12f(a)]\}^{1/2}$ is the shell charge.

Equations (6) and (7) have been put into a symmetrical form by Verma and Agarwal[25] who have critically analyzed the dielectric properties of ionic solids as described by the TSM. This analysis leads to an expression for the Szigeti effective charge,[26]

$$e_s=(1-d')e_L[1+(\lambda\alpha'/v)]^{-1}, \tag{15}$$

TABLE I. Input data.

Compounds	Lattice parameter $2a_0$ (Å)	Elastic constants 10^{12} dyn/cm^2 C_{11}	C_{12}	C_{44}	$\omega_L=\omega_T$ (10^{13} rad/sec)	α (used) (Å^3)
TaC	4.5550[a]	5.5[b]	1.2	1.6	10.8064[c]	0.39
HfC	4.64[a]	5.0[b]	0.90	1.4	8.1676[c]	0.52

[a]Reference 29. [b]Reference 4. [c]Reference 4.

where e_L is the Lundqvist effective charge,

$$e_L=\left[Z\left(Z+12f(a)+4a\frac{df(a)}{da}\right)\right]^{1/2}, \tag{16}$$

and

$$\lambda=\frac{16\pi}{3}\,\frac{Z^2}{e_L^2}\left(a\frac{df(a)}{da}\right). \tag{17}$$

d' and α', representing the distortion and electronic polarizabilities, are related to shell charges through equations similar to Eqs. (12) and (10), with e_L replacing $\{Z[Z+12f(a)]\}^{1/2}$. λ goes to zero for solids with Cauchy discrepancy zero and is usually small. Of the remaining two factors in Eq. (15), $(1-d')$ entirely depends on the distortion polarization parameter d and e_L entirely on the three-body force parameters $f(a)$ and $a[df(a)/da]$.

The dispersion curves of the transition-metal carbides do not show Lyddane-Sachs-Teller (LST) splitting between the long-wave transverse and longitudinal polar vibration frequencies ω_L and ω_T at $q=0$. This property can be directly connected to the large electrical conductivities of these solids. Imposition of the condition $\omega_L=\omega_T$ on the TSM equations directly leads to a vanishing Szigeti charge. This demands either $(1-d')=0$ or $e_L=0$. The former corresponds to an unusually large distortion polarization which is physically unrealistic. In a preliminary study we have tried both these conditions and have found that Eqs. (1)–(14) cannot be solved for $(1-d')=0$, while $e_L=0$ does not pose any such difficulty. We therefore include

$$e_L=0 \tag{18}$$

in the list of the basic equations for determining the model parameters of the carbide crystals under study. Substitution of $e_L=0$ in Eqs. (13), (14), (6), and (7) directly leads to $f_L=f_T$ and $\omega_L=\omega_T$. As suggested by Bilz[3] and by Weber *et al.*,[4] the polarizability of the carbon ion in the solids under consideration should be extremely small and can easily be neglected.

Equations (1)–(14) together with (18) represent only seven independent constraints to determine the eight model parameters in a one-ion polarizable version of the theory given above. We have therefore chosen to represent the second-neighbor short-range interaction by a single force constant A' assuming $B'=0$. In view of Eq. (18) the three-body force parameters $f(a)$ and $a[df(a)/da]$ cease to be independent and the short-range force parameter B is determined by the equilibrium condition. Thus our model is essentially a five-parameter model.

TABLE II. Model parameters.

Parameters	Values TaC	HfC
A	26.2443	27.0969
B	−0.8611	−1.2558
A'	5.9068	6.0722
$a\,\dfrac{df(a)}{da}$	−0.2148	−0.2596
Y	−1.7	−1.1
d	0.2505	0.4818

III. CALCULATION AND RESULTS

The input data for the two metal carbides are given in Table I with their original references. To obtain the best agreement with the experimental dispersion curves the values of the elastic constants C_{12} and C_{44} had to be slightly modified. The calculated values of the model parameters A, B, A',

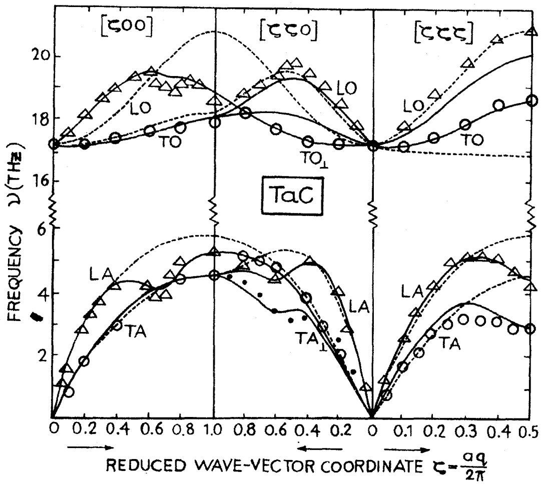

FIG. 1. Phonon dispersion curves of TaC. Triangles and circles show the experimental points (Ref. 2). Solid lines show results from a TSM calculation. Dashed lines show Mostoller's results (Ref. 6).

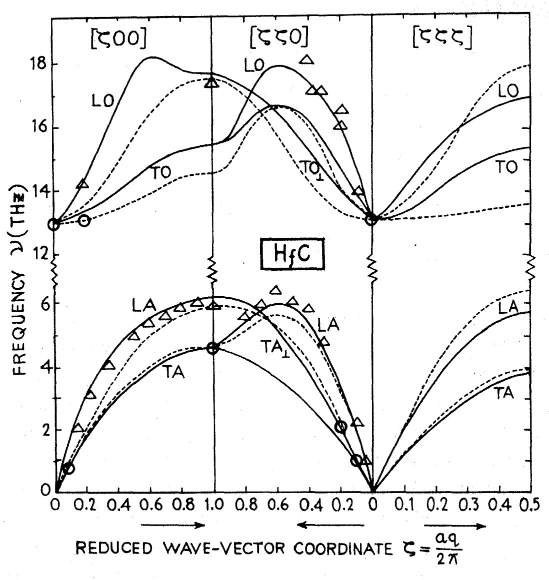

FIG. 2. Phonon dispersion curves of HfC. Triangles and circles show the experimental points (Ref. 2). Solid lines show results from a TSM calculation. Dashed lines show Mostoller's results (Ref. 6).

$a[df(a)/da]$, $d(=d_1)$, and $Y(=Y_1)$ are listed in Table II. These parameters were used for evaluating the coupling coefficients. The secular equations for the lattice vibration frequencies break in 2×2 determinants for wave vectors in the principal symmetry directions, and can be easily solved on a desk calculator. The vibration frequencies $\omega_j(\vec{q})$ so determined are plotted against q in the three principal symmetry directions and are shown by continuous lines together with experimental points of Smith and Glaser[1,2] and Smith[18] in Figs. 1 and 2. The pseudopotential-model calculations[6] are also shown in the figures by dotted curves for comparison.

It is obvious that the agreements presented by the TSM calculations are much better than the pseudopotential calculations. A comparison with Weber's curves shows that the TSM results are as good as his DSM results on TaC and the simple-screened-shell-model results on HfC. However, we could obtain these results only by using values of the polarizabilities of the metal ions about 50% higher than those quoted by Pauling.[27]

IV. DISCUSSION

The TSM formulation involves the valence Z only in expressions like $Z[Z+12f(a)]$ and $Za[df(a)/da]$, which are fixed by the input data. Variation of Z will thus lead only to different values of the parameters $f(a)$ and $a[df(a)/da]$ and will not affect the elements of the dynamical matrix. The valence Z, however, is not a very meaningful parameter in the model, the ion charges with the transferred charges being $\pm[Z+6f(a)]\simeq\pm\{Z[Z+12f(a)]\}^{1/2}$. Our calculations give $\{Z[Z+12f(a)]\}^{1/2}=0.86$ and 1.03 for TaC and HfC, respectively, which are substantially lower than the valence 4 of the ions. The values of $Z[Z+12f(a)]$ with $Z=4$ will lead to unexpectedly large negative values for $f(a)$, in which case the TSM formulas may not be accurate. It can, however, be presumed that the ions do not carry charges $\pm 4e$ but much less. This is substantiated by the values of Z obtained by Weber[4] in his calculations, which give for the carbon ion in TaC $Z=-0.71$ and in HfC $Z=-1.08$.

The resemblance between the TSM and DSM results can be easily understood by comparing the dynamical matrices derived from the two models. These matrices nearly go into each other if we identify the three-body force matrix $\underline{V}$ of the TSM by the short-range force matrix arising from the second shell of the DSM. Further, the free-electron contribution included in the dynamical matrices of both the SSM and the DSM is expressed by [Eq. (2.4) of Weber]

$$D^{sc}=4\pi Z^{\kappa}Z^{\kappa'}\frac{q_\alpha q_\beta}{q^2}\left(\frac{1}{\epsilon(q)}-1\right). \tag{19}$$

This contribution obviously affects only the longitudinal branches in the dispersion curves. The three-body force matrix also has a structure such that it affects only the longitudinal branches and can be approximated by a form similar to Weber's (2.4).[28] Even though the meanings of the disposable parameters may be somewhat different in the two formulations, in a phenomenological theory the TSM may lead to results similar to SSM and DSM.

The resonance effect in the DSM supposed to explain the anomalous wiggles in high-T_c transition-metal carbides[4] is not obvious in the TSM formulation. We may point out here that even in the simple shell model one generally obtains dips in the longitudinal acoustic branches near the zone boundary in the $[q,\ 0,\ 0]$ direction. While such dips appear in all shell-model calculations concerning the alkali halides, they are completely absent from the calculations on the alkaline-earth oxides. The reason for this difference of behavior in the two systems is obviously not due to the model, but to the values of the physical properties used as input data. In view of this observation we can possibly understand the difference in the nature of the dispersion curves of the two solids TaC and HfC as predicted by the TSM.

ACKNOWLEDGMENT

We are thankful to Dr. W. Weber for having sent us his results before publication.

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