# Lattice Dynamics of Transition-Metal Carbides

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The phonon dispersion relations of ZrC, NbC, HfC, TaC, and UC are investigated using a phenomenological-model theory. For the transition-metal carbides, a shell model with a free-electron screening is used to describe the over-all shape of the phonon curves. The results strongly support the "covalent model," where the extreme physical properties of these compounds are attributed mainly to strong covalent metal-nonmetal bonding. In contrast, for UC the "interstitial-alloy" picture seems to be more appropriate. The pronounced anomalies in the acoustic branches of TaC and NbC occur at certain  $\vec{q}$  values which are directly related to definite lattice vectors. We interprete the anomalies as originating from a resonancelike increase of the electronic polarizability due to strong short-range correlations of the d conduction electrons. In a model theory, we represent this d charge density by a further electronic degree of freedom at the metal-ion sites, i.e., a second shell. Calculations with this "double-shell model" show very good agreement with experimental data. It is strongly indicated that the anomalies are caused by d electrons of  $T_{2g}$  symmetry. The connections to structural phase transitions are discussed.

### **J. INTRODUCTION**

The phonon dispersion curves of transition-metal carbides have recently been measured by Smith and Gläser.<sup>1-3</sup> Some of these substances exhibit strong anomalies in a limited part of the Brillouin zone. In this paper we will treat the lattice dynamics of the transition-metal carbides by using a phenomenological-model theory. We will direct our attention especially to the anomalies in the phonon spectra.<sup>4</sup> We interpret them as a resonancelike increase of the electronic polarizability. This effect is described by a specific extension of the shell model. The connection between phonon anomalies and superconductivity will be discussed in the following paper.<sup>5</sup>

The carbides and nitrides of the group-IV, -V, and -VI transition metals show an unusual combination of physical properties.<sup>6</sup> Their melting points and hardnesses are very high, similar to homopolar diamond. In the other hand, they are good metals and many of them are superconductors with very high transition temperatures. Most of the compounds have NaCl structure, but hexagonal and more complex crystal geometries are also found. Furthermore, in many compounds, there exists a wide nonstoichiometric range in the composition, in which the lattice structure remains unchanged.

There are two models for the chemical bonding of the transition-metal compounds under discussion. The older one originates from Hägg, <sup>7</sup> who introduced the name "interstitial" compounds, describing the idea that the small nonmetal atoms fill the empty regions of the metal host lattice. This concept suggests that the physical properties are dominated by the metallic bonding. Furthermore, the fact that the conductivities, the hardnesses, and the melting points of the compounds often exceed those of the metals is attributed to an electron transfer from the nonmetal atoms to the metal conduction bands.<sup>8</sup> We will call this model the "interstitial-alloy" model.

The other model postulates a covalent metalnonmetal interaction to be essential for the stability of the compounds. Bilz<sup>9</sup> was the first who realized the importance of this idea for a bandstructure calculation for TiC, TiN, and TiO using the linear-combination-of-atomic-orbitals (LCAO) method and assuming a rigid-band model. He obtained low-lying bands of bonding character which are formed by nonmetal p states and mainly metal d states of  $E_{e}$  symmetry. This feature is connected with an electron transfer to the nonmetal atoms. Metallic d bands of  $T_{2g}$  symmetry lie above those and partially overlap. In crystals with eight valence electrons (VE) per unit cell (e.g., TiC, ZrC, HfC) all the bonding p-d states are occupied and the density of states at the Fermi surface is minimal. In compounds with a higher number of VE (e.g., TiN, TiO) the metallic d bands will progressively fill and the density of states at the Fermi energy will increase rapidly.

More refined band-structure calculations,  $^{10-14}$  using the augmented-plane-wave (APW) method, are in good qualitative agreement with these results. They show that a rigid-band model approximately holds good for all the compounds with cubic structure and that there *is* some electron transfer to the nonmetal ions.

Experimentally the "covalent" model is confirmed by measurements of the magnetic susceptibility<sup>15</sup> and the electronic specific heat, <sup>16</sup> which vary proportionately with the density of states at the Fermi energy. Furthermore, the superconducting transition temperature increases rapidly from compounds with eight VE to those with nine

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and ten.<sup>6,17</sup> It does not matter very much whether the number of VE is changed by variation of the metal or the nonmetal atoms.

The phonon dispersion relations of group-IV and -V transition-metal carbides (TMC) have been measured by Smith and Gläser<sup>1-3</sup> (see Figs. 4-7). TaC and NbC show strong anomalies in a limited region of the Brillouin zone, in contrast to ZrC and HfC, where no anomalies exist. These anomalies will be discussed in detail later.

In their over-all shapes, however, the phonon spectra are rather similar. The high values of the elastic constants (see Table I) show up in the steep rise of the acoustic branches. The optic modes are separated by a very large gap from the acoustic ones and are split largely at shorter wavelengths, which indicate a certain amount of ionic interaction. The splitting is removed near  $\vec{q} = 0$ , where the longitudinal-optic (LO) branches show a strong dispersion. The LO and TO (transverse-optic) modes are degenerate at  $\vec{q} = 0$ , since all the compounds are conductors.

In contrast, the phonon spectrum of metallic UC is rather different<sup>3</sup> (see Fig. 8). Here the optic branches lie about 30-50% lower than those of the TMC. They are not separated very much and show little dispersion throughout the Brillouin zone. Thus, the very high optic frequencies of the transition-metal carbides are due not only to the large mass difference of the atoms but also to much stronger force constants between nearestneighbor metal and nonmetal ions. This supports the idea that the binding in these carbides is strongly covalent with some ionic contribution. In the optic modes the metallic character of the

TABLE I. Lattice parameters and elastic constants of transition-metal carbides.

	$r_0$	<i>C</i> <sub>11</sub>	<i>C</i> <sub>12</sub>	C <sub>44</sub>
	(Å)	<b>(</b> ×:	10 <sup>12</sup> dyn/cm	<sup>2</sup> )
TiC	2.16ª	5.1 <sup>b</sup>	1.0	1.8
ZrC	2.35	4.7 <sup>b</sup>	1.0	1.6
HfC	2.32	5.0°		1.8
VC <sub>0,84</sub>	2.08	5.0 <sup>b</sup>	2.9	1.5
NbC	2.235	6.2°	2.0	1.5
TaC <sub>0,90</sub>		5.0 <sup>b</sup>	0.9	0.8
TaC	2.228	5.5°	1.5	1.9
UC	2.48	3.2 <sup>d</sup>	0.86	0.65

<sup>a</sup>All lattice parameters are taken from Ref. 6.

<sup>d</sup>L. J. Graham, J. Nadler, and R. Chang, J. Appl. Phys. <u>34</u>, 1572 (1963). compounds manifests itself only in the screening of the macroscopic electric fields at long wavelengths, which drastically influences the LO modes near  $\vec{q} = 0$ .

In Sec. II we review the shell model,<sup>18</sup> which has been proved to work satisfactorily for ionic and covalent crystals.<sup>19-21</sup> This model, therefore, is used to calculate the over-all shapes of the phonon spectra. To describe the LO modes at long wavelengths, the shell model is modified by adding a free-electron-like screening term.

In Sec. III the phonon anomalies in TaC and NbC are considered in more detail. An analysis of their position will show a certain phase dependence which indicates short-range correlations. We then present a model which describes the very-longrange ion-ion forces (which give rise to the soft modes) by a short-range ion-electron-ion interaction (Sec. IV). The results of our calculations both for the transition-metal carbides and for UC are given in Sec. V. These are discussed in Sec. VI, especially in connection with the electronic properties.

## **II. SHELL MODEL WITH FREE-ELECTRON SCREENING**

To describe the over-all shapes of the spectra, we have used a simple shell model; i.e., we assume all forces are acting through the shells. In the harmonic, adiabatic and electrostatic approximation, the equations of motion  $are^{19,20}$ 

$$\underline{\mathbf{m}}\omega^{2}\underline{\mathbf{u}} = (\underline{\mathbf{R}} + \underline{\mathbf{Z}}\underline{\mathbf{C}}\underline{\mathbf{Z}})\underline{\mathbf{u}} + (\underline{\mathbf{R}} + \underline{\mathbf{Z}}\underline{\mathbf{C}}\underline{\mathbf{Y}})\underline{\mathbf{w}}, \qquad (2.1)$$

$$\mathbf{0} = (\mathbf{R} + \mathbf{Y} \mathbf{C} \mathbf{Z})\mathbf{u} + (\mathbf{k} + \mathbf{R} + \mathbf{Y} \mathbf{C} \mathbf{Y})\mathbf{w} . \qquad (2.2)$$

Here the hypervectors  $\underline{u}$  and  $\underline{w}$  denote the displacements of the ions and the relative core-shell displacements, respectively. <u>R</u> and <u>C</u> are the matrices of the short-range and the Coulomb force constants. The elements of <u>R</u> are given in the Appendix. The diagonal matrices <u>Z</u>, <u>Y</u>, <u>k</u>, and <u>m</u> denote, respectively, the ion charges, shell charges, core-shell force constants, and the masses of the ions. The adiabatic approximation is expressed by having put the electron mass equal to zero on the left-hand side of Eq. (2.2). Thus we are able to eliminate the electronic degrees of freedom w and obtain the dynamical matrix:

$$\frac{\phi}{\Phi} = (\mathbf{R} + \mathbf{Z} \mathbf{C} \mathbf{Z}) - (\mathbf{R} + \mathbf{Z} \mathbf{C} \mathbf{Y}) \\
\times (\mathbf{k} + \mathbf{R} + \mathbf{Y} \mathbf{C} \mathbf{Y})^{-1} (\mathbf{R} + \mathbf{Y} \mathbf{C} \mathbf{Z}) .$$
(2.3)

We wish to point out that the elastic constants are given by the first term of Eq. (2.3); i.e., they are not affected by the polarizability of ions represented by shell-core displacements.

The influence of conduction electrons on the longitudinal-optic branches at long wavelengths is taken into account by assuming that a few free electrons produce a screening. This gives the

<sup>&</sup>lt;sup>b</sup>Reference 6.

<sup>&</sup>lt;sup>c</sup>Extrapolated from neutron data of Refs. 1-3.

following contribution to the dynamical matrix:

$$D_{ij}^{\rm sc}(\kappa\kappa';\vec{q}) = 4\pi Z_A^{\kappa} Z_A^{\kappa'} - \frac{q_i q_j}{q^2} \left(\frac{1}{\epsilon(q)} - 1\right), \qquad (2.4)$$

with

$$(q) = 1 + \frac{1}{q^2} \times \left( \frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right).$$
(2.5)

Here  $k_F$  is the Fermi wave vector, and the Thomas-Fermi screening vector  $k_s$  is given by

$$k_s^2 = \frac{4k_F(m^*/m)}{2r_0\pi} , \qquad (2.6)$$

where  $m^*$  is an effective electron mass.

 $k^2$ 

These formulas are very similar to those of Ref. 21. The charge  $Z_A$  is determined by the condition  $\omega_{\rm LO} = \omega_{\rm TO}$  for  $\vec{q} = 0$ ; and  $k_s$  and  $k_F$  are found by a least-squares fit to the LO branches. Their values do not differ very much for the compounds under consideration. Therefore, we always put  $k_s = k_F = 0.4(\pi/r_0)$ . This value of  $k_F$  corresponds to a free-electron density of  $n_{\rm el} \simeq 0.1$  per unit cell.

It is found that the dispersion curves of ZrC and HfC, and the over-all shapes of the TaC and NbC spectra, are described quite well by the shell model including the screening term (see Sec. V for details).

### **III. ANOMALIES IN THE PHONON SPECTRA**

As mentioned above, TaC and NbC show sharp minima in most of the acoustic branches, which, however, are found neither in ZrC and HfC nor in  $NbC_{0.75}^{2}$  (see Figs. 4-7). Similar anomalies appear in the phonon spectra of the bcc Nb-Mo system<sup>22</sup> and in homologous transition metals: In Mo a sharp minimum is found at the H point (1, 0, 0)of the Brillouin zone. When up to 25-at.% Nb is alloyed with Mo, this minimum disappears. When the Nb concentration is increased further, other minima appear in the longitudinal branches, which lie at  $\xi \approx 0.7$  both in the  $(\xi, 0, 0)$  and  $(\xi, \xi, \xi)$  directions. Simultaneously, the elastic constant  $c_{44}$ tends to zero. These soft modes are not related to Kohn anomalies which are also observed in these materials. The soft modes are considerably stronger than the Kohn anomalies. Further, it is observed that the soft modes always appear and disappear at the same position in  $\overline{\mathbf{q}}$  space. In contrast, the position of the Kohn anomalies show a strong q dependence with Nb concentration.

In the transition-metal compounds NbC and TaC, the anomalies also appear in the acoustic parts of the phonon spectra, where the dynamics are dominated by the heavy metal ions. The soft-mode regions are found in all acoustic branches except those which propagate along the  $(\xi, 0, 0)$  and  $(\xi, \xi, 0)$  directions, and are polarized along  $(0, 0, \xi)$ . In the long-wavelength limit these branches determine the elastic constant  $c_{44}$  (see Figs. 4 and 5). The minima lie in the set of directions  $(\xi, 0, 0)$  at  $\xi_m = 0.65 \approx 0.5$ ; in  $(\xi, \xi, 0)$  at  $\xi_m = 0.55 \approx 0.5$ , and in  $(\xi, \xi, \xi)$  at  $\xi_m = 0.5$ . When we put  $\xi_m = 0.5$ , the set of planes  $\{\xi_m 00\}$  are the faces of a cube, the corners of which touch the first Brillouin zone at the eight L points. The real soft-mode region would form the surface of a cubelike body swollen on the  $\{\xi 00\}$  faces.

The cube in reciprocal space (see Fig. 1) corresponds to simple-cubic sublattices of the fcc metal lattice. The crystal tends to become unstable for such phonons where nearest neighbors of the simple-cubic sublattices vibrate in opposite phases, e.g., for  $\vec{q} = (\frac{1}{2}, 0, 0)$ ,  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (see Fig. 2). Therefore, one might assume a strong interaction of nearest-neighbor ions of the simple-cubic sublattices (i.e., second neighbors of the fcc lattice). Their contribution to the dynamical matrix has the  $\vec{q}$  dependence

$$\phi_{ii}^{200}(\mathbf{q}) \propto (1 - \cos(2q_i r_0) = 2 \sin^2(q_i r_0)),$$

which is of maximum strength just on the surface of the cube. Furthermore, an addition of nearestneighbor force constants would shift the maxima in the  $(\xi, 0, 0)$  and  $(\xi, \xi, 0)$  directions towards the zone boundary. However, the crystal lattice tends to become unstable in a "resonance like" manner, since the width of the soft-mode region is rather small, and therefore a Fourier analysis of the phonon curves shows that force constants between very distant neighbors (about 20 net planes) have to be included for a satisfactory description of the phonon curves.<sup>1,22</sup> Also, we could not describe the dispersion curves of TaC and NbC by using a



FIG. 1. Brillouin zone of the fcc lattice. Dashed lines represent the "resonance cube."



FIG. 2. Pattern of motion for the acoustic phonon with  $\bar{q} = (\frac{1}{2}, 0, 0)$ . The distribution of the charge density is indicated for the metallic *d* electrons with  $T_{2g}$  symmetry.

shell model. Even if we removed the assumption that the forces act through the shells only, and if we further introduced force constants to more distant neighbors, i.e., even if we used about 20 disposable parameters, we could not find good agreement with the experimental curves.

#### **IV. "DOUBLE-SHELL" MODEL**

We think the very-long-range forces between the metal ions are of electronic orgin. On the basis of energy-band calculations<sup>9-14</sup> we expect that the main difference between the IV B-IV A and V B-IV A compounds is a new d band which is partially filled in TaC and NbC, while it is empty in the IV B-IV A compounds ZrC and HfC. It is plausible that these d electrons cause the anomalies.

However, we failed in describing their influence by introducing additional force constants into the shell model. Instead, we introduce an additional electronic degree of freedom which is to represent the *d*-electron charge density. An extra shell of electrons (a "supershell") is assumed to move in the potential due to the metal-ion core plus inner shell, and to interact with neighboring supershells (see Fig. 3). This is parametrized by a coreshell coupling constant k' and a force-constant matrix  $\underline{\mathbf{R}}'$ . Our results show that short-range interactions between first and second neighbors in the electronic system cause the very-long-range ionion forces.

Now we derive the equations of motion for this "double-shell" model (DSM). When we denote the displacements from the lattice sites by the hypervectors  $\underline{u}$ ,  $\underline{s}$ , and  $\underline{s}'$  for the ion cores, the inner shells, and the outer shells, respectively, we get

$$\underline{m}\omega^2 \underline{\mathbf{u}} = \underline{\mathbf{k}}\,\underline{\mathbf{u}} - \underline{\mathbf{k}}\,\underline{\mathbf{s}} , \qquad (4.1)$$

$$0 = -\underline{\underline{k}}\underline{\underline{u}} + (\underline{\underline{k}} + \underline{\underline{k}}' + \underline{\underline{R}})\underline{\underline{s}} - \underline{\underline{k}}'\underline{\underline{s}}', \qquad (4.2)$$

$$0 = -k's + (k' + R')s'. \qquad (4.3)$$

For sake of simplicity we have omitted the electrostatic interactions. We then transform to relative core-shell displacements

$$\frac{\mathbf{w}=\mathbf{s}-\mathbf{u}}{\mathbf{w}'=\mathbf{s}'-\mathbf{u}}, \qquad (4.4)$$

and add Eqs. (4.2) and (4.3) to Eq. (4.1), thus giving

$$\underline{\mathbf{m}}\omega^{2}\underline{\mathbf{u}} = (\underline{\mathbf{R}} + \underline{\mathbf{R}}')\underline{\mathbf{u}} + \underline{\mathbf{R}}'\underline{\mathbf{w}}', \qquad (4.5)$$

$$0 = \underline{\mathbf{R}} \underline{\mathbf{u}} + (\underline{\mathbf{k}} + \underline{\mathbf{k}}' + \underline{\mathbf{R}}) \underline{\mathbf{w}} - \underline{\mathbf{k}}' \underline{\mathbf{w}}', \qquad (4.6)$$

$$\mathbf{D} = \mathbf{\underline{R}'} \underline{\mathbf{u}} - \mathbf{\underline{k}'} \underline{\mathbf{w}} + (\mathbf{\underline{k}'} + \mathbf{\underline{R}'}) \underline{\mathbf{w}'}. \tag{4.7}$$

When we eliminate the electronic degrees of freedom  $\underline{w}$  and  $\underline{w}'$  by using the adiabatic approximation and restore the electrostatic interactions as well as the screening term [see Eq. (2.4)], we are led to the following dynamical matrix:

$$\underline{\phi} = \underline{\tilde{\mathbf{R}}} + \underline{Z} \underline{C} \underline{Z} + \underline{D}^{sc}$$

$$- (\underline{\tilde{\mathbf{R}}} + \underline{Z} \underline{C} \underline{Y}) (\underline{\mathbf{k}} + \underline{\tilde{\mathbf{R}}} + \underline{Y} \underline{C} \underline{Y})^{-1} (\underline{\tilde{\mathbf{R}}} + \underline{Y} \underline{C} \underline{Z}),$$

$$(4.8)$$

where

$$\frac{\tilde{\mathbf{R}}}{\mathbf{R}} = \mathbf{R} + \mathbf{R}' - \mathbf{R}' (\mathbf{k}' + \mathbf{R}')^{-1} \mathbf{R}'$$
$$= \mathbf{R} + \mathbf{k}' (\mathbf{k}' + \mathbf{R}')^{-1} \mathbf{R}' . \qquad (4.9)$$

Electrostatic interactions between the supershells are neglected. Furthermore, we do not introduce the new electronic degree of freedom  $\underline{w}'$  at the carbon ions. This can be described formally by putting  $1/k'_c = 0$  in order to maintain the convenient matrix notation. The elements of the matrix  $\underline{\mathbf{R}}'$ are given in the Appendix.

The elastic constants are now determined by the expression  $\underline{R} + \underline{Z} \underline{C} \underline{Z} + \underline{R}'$ . However, when going from HfC to TaC, they remain practically unchanged. So, the relation

$$||\underline{\mathbf{R}}'||/||\underline{\mathbf{R}}+\underline{\mathbf{ZC}}\,\underline{\mathbf{Z}}||\ll 1 \tag{4.10}$$

has to be valid. To get instabilities for a certain  $\vec{q}$  regime the condition



FIG. 3. Double-shell model.

must hold.

On the one hand we find that  $\underline{\mathbf{R}}'$  should be rather small, while on the other hand the term  $\underline{\mathbf{k}}'$  $\times (\underline{\mathbf{k}}' + \underline{\mathbf{R}}')^{-1} \underline{\mathbf{R}}'$  has to be very large, negative, and rapidly varying with  $\overline{\mathbf{q}}$  in order to cancel the slowly varying term  $\underline{\mathbf{R}}(\overline{\mathbf{q}})$  in the soft-mode region. To fulfill these conditions,  $(\underline{\mathbf{k}}' + \underline{\mathbf{R}}')$  must behave like a resonance denominator which becomes very small in the critical  $\overline{\mathbf{q}}$  regime:

$$\mathbf{k'} + \mathbf{R'}(\mathbf{\bar{q}}) \stackrel{>}{\simeq} \mathbf{0} \ . \tag{4.12}$$

This holds only if the force constants entering the matrix  $\underline{\mathbf{R}}'$  are negative; i.e., if the forces between the supershells are attractive. So the new electronic degree of freedom represents a charge density which is rather weakly bound at the metal ions and is in an unstable position with respect to displacements of neighboring charge densities. If the condition (4.12) holds for certain  $\overline{\mathbf{q}}$  values, the crystal tends to a resonancelike increase of the polarizability and to a sudden softening of the phonon frequencies.

We want to note that the equations of motion of



FIG. 4. Phonon dispersion curves of NbC. Triangles and circles show the experimental values (Ref. 2). Solid lines show the results obtained from DSM. For comparison, the dashed lines show the same model without the second-shell contribution. The dotted lines show the calculated LO branches without screening term.



FIG. 5. Phonon dispersion curves of HfC. Triangles and circles show experimental values (Refs. 1 and 2). Solid lines are the results from SM calculation with freeelectron screening term. For comparison, the optical branches of TaC are shown by dotted lines. Dashed lines are Mostoller's results (Ref. 28).

the "double-shell" model are not quite the same as those of the model given in I, where the degree of freedom  $\underline{w}_1$  is not explicitly attributed to a displacement of the *d*-electron charge density. In both models, however, a resonancelike denominator appears in the dynamical matrix, and the quality of the calculations is equally good, and the force constants are practically the same.

# V. RESULTS

The phonon dispersion relations of NbC and TaC are calculated using the DSM (see Figs. 4 and 7). This model was also applied for the phonon spectra of the Nb-Mo system; these calculations are discussed elsewhere.<sup>23</sup> A shell model with a free-electron screening term is used for HfC and ZrC (see Figs. 5 and 6), while the phonon curves of UC are analyzed by a shell model without a screening term (see Fig. 8). The model parameters are determined by a least-squares fit to the experimental data. We obtained always a unique set of parameters (see Tables II and III).

For ZrC and NbC the densities of states of the acoustical phonons are shown in Fig. 10. Because of the soft-phonon modes, the density of states of

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FIG. 6. Phonon dispersion curves of ZrC. Triangles and circles show experimental values (Refs. 3 and 24). Solid lines are the results of a shell-model calculation with screening term. The parameters have been determined without any knowledge of the optical frequencies except  $\omega_{TO}$  at  $\Gamma$ .

NbC differs rather drastically from that of ZrC.

As shown in Fig. 4 (NbC) the shell-model (SM) contribution describes the over-all shapes of the curves, while the screening term only affects the LO branches near the  $\Gamma$  point of the Brillouin zone. The addition of the second shell contributes strongly in the soft-mode regions and is almost imperceptible elsewhere.

## A. SM with Screening

About eight SM parameters are used for the transition-metal carbides (see Table II). This number is comparable with that needed for alkali halides. The nearest-neighbor force constants A(12) and B(12) are very strong, while the nextnearest-neighbor ones,  $A_1(22)$  and  $B_1(22)$ , which act between the metal ions, are about half of their size. These force constants are taken to be axial symmetric; the curves are affected very little by this assumption.

Further important parameters are the ionic charge Z, the core-shell force constants  $k_1$  and  $k_2$ , and the shell charge  $Y_2$ . The carbon polarizability and the force constants between nearest-neighbor

carbon atoms, which essentially influence only the optic branches, turn out to be rather small. We therefore put  $Y_1$ ,  $A_1(11)$ , and  $B_1(11)$  equal to zero.

The SM parameters of HfC and ZrC are determined without specific knowledge of the optic branches. Especially, the optic phonons of ZrC except for the  $\Gamma$ -point frequency were unknown at the time the calculations were carried out. The results are in good agreement with recent measurements by Smith.<sup>24</sup>

The short-range force constants of HfC and ZrC (IVB-IVA) and of NbC and TaC (VB-VIA) are almost equal, while HfC and ZrC have higher ionic charges and polarizabilities as compared to NbC and TaC. In all compounds, the screening parameters  $k_s$  and  $k_F$  are put equal to  $0.4(\pi/r_0)$ .

In contrast to the transition-metal carbides, the ionic charge and the polarizability of UC is negligibly small (see Table II). Furthermore, the nearest-neighbor metal-carbon force constants are much weaker. However, there is a small, but not negligible, C-C interaction. This is responsible for the dispersion in the optic branches, which



FIG. 7. Phonon dispersion curves of TaC. Triangles and circles show the experimental values (Ref. 1). Solid lines show results from a DSM calculation. The dotted lines show a calculation with  $C'_1 = \frac{1}{2}B'_1$ . In (0, 0,  $\xi$ ) the curves are not affected by a variation of  $C'_1$ . The dashed lines show Mostoller's results for the optical branches of TaC.



FIG. 8. Phonon dispersion curves of UC. Triangles and circles show experimental values (Ref. 3). Solid lines are the results of a shell-model calculation. Our shell-model fit is of about the same quality as that shown in Ref. 3.

is rather strong in spite of the large mass ratio. We want to comment on the dip in the TO branch in  $(\xi, \xi, 0)$  at  $\xi \approx 0.6$  which we could not completely reproduce by our fit (see Fig. 8), although we included second- and fourth-nearest-neighbor C-C force constants (see Table II). We think that this distant-neighbor C-C interaction may indicate the existence of U deformabilities.

#### **B.** Soft-Mode Region

The DSM reproduces the "resonance cube" of NbC and TaC (see Figs. 4 and 7). Very good agreement is obtained for the acoustic branches. The minimum in the lower TA branch in the  $(\xi, \xi, 0)$  direction, which was predicted in I, has now been verified experimentally.<sup>25</sup> There are only minor discrepancies in the dispersion curves, especially

the fact that the anomalies which appear to a certain extent in the LO  $(\xi, 0, 0)$  branch are reproduced too weakly.

As was mentioned above, the additional electronic degrees of freedom were introduced at the metal sites only; therefore, all coupling constants (distinguished by primes in the following) describe interactions in the metal sublattice. The longitudinal force constants  $A'_1$  and  $A'_2$  between nearest and next-nearest "supershells" determine the position of the anomalies within the Brillouin zone.  $A'_2$  alone makes the minima lie exactly on the surface of the cube of Fig. 1; the addition of  $A'_1$  shifts the position of the minima in  $(\xi, 0, 0)$ , and to a lesser extent in  $(\xi, \xi, 0)$ , towards the zone boundary. The width of the soft-mode region is mainly determined by the size of the core-shell coupling constant k', which then scales the magnitude of the different force constants because of the condition (4.12). The transverse nearest-neighbor force constant  $B'_1$ , which acts in the cube plane, is necessary to adjust the depths of the minima in the different symmetry directions relative to each other. Minor corrections are given by  $B'_2$ .

We found that the best fits always gave very nearly  $A'_2: A'_1: B'_1=4:3:2$ . Since the DSM describes a resonancelike increase of the electronic contribution to the dynamical matrix, the dispersion curves are very sensitive to the choice of parameters. It is therefore particularly interesting that the transverse force constant  $C'_1$  between nearest neighbors, which acts perpendicular to the plane, turns out to be zero. To demonstrate how much a variation of  $C'_1$  changes the curves, a calculation is shown where  $C'_1$  is put equal to  $\frac{1}{2}B'_1$ without any change of the other parameters (see Fig. 7).

#### VI. DISCUSSION

For the TMC, there are very strong nearestneighbor force constants A(12) and B(12). In UC,

TABLE II. Shell-model parameters; force constants are given in units of  $e^2/2r_0^3$ , the charges in units of the elementary charge. The numbers 1 and 2 in brackets refer to carbon and metal ions, respectively; the subscripts *n* refer to *n*th-order neighbors in the fcc sublattice.

	Fig.	A (12)	B(12)	A <sub>1</sub> (22)	B <sub>1</sub> (22)	Z(1)	Y(1)	Y(2)	k <sub>1</sub>	k2
NbC	4	19.62	3.96	9.02	-0.70	- 0.696	0	-1.6	726	145
HfC	5	22.50	4.60	13.08	-1.77	-1.08	0	-1.3	180	107
ZrC	6	23.82	3.47	10.02	-1.02	-1.08	0	-2.0	309	123.5
TaC <sup>a</sup>	•••	21.65	4.54	10.53	-1.1	-0.71	0	-1.2	469	145
TaC	7	21.83	4.19	9.58	-1.1	-0.66	0	-1.2	469	145
UC <sup>b</sup>	8	11.82	1.20	10.57	-0.436	0	0	0	479	647

<sup>a</sup>Best-fit values for TaC.

<sup>b</sup>For UC we put  $A_2(11) = 2A_1(11) = 0.42$ ,

 $B_2(11) = 2C_1(11) = -0.30, B_1(11) = 0.$ 

		the second s					
	Fig.	A'1	<i>B</i> ' <sub>1</sub>	Cí	Aş	Bź	k'
NbC	4	-0.713	-0.484	0	-0.943	-0.136	6.0
TaC <sup>a</sup>	•••	-0.96	-0.64	0	-1.30	-0.12	8
TaC	7	-0.987	-0.658	•••	-1.371	-0.137	8.53
" NbN " <sup>b</sup>	•••	-1.15	-0.80	0	-1.66	-0.18	10.0

TABLE III. DSM parameter for the transition-metal carbides (in unts of  $e^2/2r_0^3$ ). The subscripts *n* refer to *n*th-order neighbors in the fcc sublattice.

<sup>a</sup>Best-fit values for TaC.

<sup>b</sup>Parameters of an almost unstable crystal, for which the density of states is shown in Fig. 10.

however, the metal-carbon interaction is much weaker. Furthermore, we get the result that the carbon ions in the TMC are negatively charged, while in UC there is no evidence for ionic bonding at all. The special properties of the TMC, viz., their hardness, brittleness, and high melting point, are due to very strong covalent bonding between metal and nonmetal atoms. The effect of metallic bonding is less important but not negligible. It causes force constants between nearestneighbor metal ions which are necessary to obtain a good fit to the acoustic branches. Therefore, the analysis of the phonon dispersion curves rather clearly confirms the "covalent" model. On the other hand, the "interstitial-alloy" model seems to be more appropriate to UC, since it is expected to give rather low-lying and flat optic branches.

The decrease of ionic charge when going from the IV B-IV A to the V B-IV A compounds is in agreement with x-ray results<sup>26</sup>; moreover, the change of polarizability is also found in optic measurements.<sup>27</sup>

The higher values, both of the ionic charge and of the polarizability, influence the optic modes of the IV B-IV A compounds rather strongly. While an increase of the latter decreases the average optic frequencies, an increment of charge lowers the transverse-optic modes, especially at the  $\Gamma$ point. The large decrease of  $\omega_{TO}$  in HfC and ZrC as compared to TaC and NbC can thus be explained, and so it is not necessary (as was done in I) to assume a similar mechanism as for the acoustic soft modes.

In a recent publication, Mostoller<sup>28</sup> tried to reproduce the over-all features of the phonon spectra of the transition-metal carbides by a simple dielectric response approach which uses Heine-Abarenkov pseudopotentials and free-electron screening. For comparison we show Mostoller's results for HfC and TaC (see Figs. 5 and 7). Although he used seven parameters, which is comparable to our eight SM parameters, his results seem to be inferior to our shell-model calculations. Especially for TaC the optic branches do not agree very well, presumably because his model does not take the ionic interaction into account. Furthermore, in his calculation for HfC, the slopes of the LA branches near  $\bar{q} = 0$  are too low, i.e., the calculated value of the elastic constant  $c_{11}$  would be about half of the experimental value, while our results agree with the experimental data within experimental error.

The "covalent model" postulates that metallic d states of  $T_{2g}(xy)$  symmetry become filled as we go from compounds with eight VE to those with nine and ten,<sup>29</sup> and our model calculations strongly support this statement. In the DSM the transverse force constants to nearest neighbors in the fccmetal sublattice,  $B'_1$  and  $C'_1$ , are rather different;  $C'_1$ , which acts perpendicularly to the xy plane, turns out to be zero. This zero seems very precise, since the dispersion curves are very sensitive to  $C'_1$  (see Fig. 7). It is rather suggestive that deformations of charge densities having xy symmetry exclude a coupling perpendicular to the xy plane in first approximation. Also, we may interpret the force constants  $A'_2$  and  $B'_2$  as being due to interactions of the  $d(T_{2s})$  electrons, when we assume angular forces. Table IV shows how various valence-field force constants<sup>30</sup> transform to Cartesian ones. The ratio of  $A_2'/B_2'$  is given rather well by the valence-field force constant  $(\Delta \phi)$   $(\Delta \phi')$ (see Fig. 9). One may conclude that the soft modes originate mainly from an angular instability in the d charge density.

We should mention that various mechanisms have been postulated in trying to explain the phonon anomaly in the  $(\xi, 0, 0)$  longitudinal branch of Nb, which is very similar to those in NbC and TaC.<sup>31,32</sup> In these mechanisms, however, the special  $\bar{q}$  dependence of the phonon anomalies manifest in the existence of the "resonance cube" in the TMC, is not brought out.

The elements of the dynamical matrix are strongly reduced in the anomalous regions: At the L point their values are only about 30% of the

TABLE IV. Transformation of valence-field force constants to Cartesian force constants in a fcc lattice. The columns labeled 1 and 2 denote first and second neighbors, respectively. Only the ratios of the force constants are indicated.

	<b>1</b> µ v о v µ о	<b>2</b> αοο οβο
(Δ1) <sup>2</sup> 1	1 1 0 1 1 0 0 0 0	
	-	4 0 0 0 -2 0 0 0 -2
$(\Delta \Phi)^2 \qquad \Phi$	4 -4 0 -4 4 0 0 0 0	-4 0 0 0 2 0 0 0 2
$(\nabla \Phi)(\nabla \Phi_i)$	-4 -4 C -4 -4 O O O O	10 0 0 0 1 0 0 0 1

shell-model values. In a rough approximation we assume that the magnitude of the additional DSM contribution is proportional to the density of the  $d(T_{2g})$  electrons; furthermore, we fix the ratio of the force constants involving the second shell. We then obtain a phonon instability at the *L* point at about 9.5 VE in the TaC system, while for the NbC system, where the anomalies are less strong, the phonons may be stable up to 10 VE : A phase transition from the fcc to the hcp structure occurs in the TaC<sub>x</sub>-N<sub>1-x</sub> systems near x = 0.4, <sup>33</sup> while NbC<sub>x</sub>-N<sub>1-x</sub> for all x is still cubic.<sup>6</sup>

Such a phase transition may occur via a soft mode at the L point. The transverse-acoustic modes are shear modes of close-packed metal planes, which then may slip easily from  $ABCA \cdots$ to  $ABAB \cdots$  sequences. We point out that hardness measurements show {111} slip planes in TaC but not in HfC.<sup>34</sup>

The soft modes are stabilized by anharmonic interactions<sup>1</sup> and the frequencies in the soft-mode regions increase with increasing temperature. Crystals as MoC, WC, and TaN, which are unstable in the cubic phase at room temperature, have NaCl structure at high temperature.<sup>6</sup> We may understand this within the quasiharmonic approximation, if we assume that the DSM force constants, as other force constants, become weaker with increasing temperature. The resonance denominator in Eq. (4.11) then becomes larger with increasing temperature and the DSM contribution to the dynamical matrix decreases, leading to a stable system at higher temperatures.

The density of states of the acoustic phonons is influenced rather strongly by the appearance of the soft modes in the dispersion curves. This may be seen from Fig. 10, where the phonon densities of states of ZrC and NbC are shown. Also given here is the phonon density of an almost unstable crystal ("NbN"), for which a rapid increase of the density is found very near to  $\omega = 0$ . This rather high density at low phonon frequencies influences the low-temperature behavior of the lattice specific heat. Debve's  $T^3$  law, which is due to the long-wavelength acoustical phonons, should be valid only in a very small temperature region  $(T \simeq 4$  °K). At slightly higher temperatures this contribution should be overshadowed by that due to the low-frequency phonons of the anomalous regions near the zone boundary. Their contribution to the lattice specific heat increases exponentially with temperature in a manner very similar to the Einstein model.

There is the question whether the adiabatic approximation still holds in the soft-mode regions. When putting the shell mass equal to the electronic mass in the shell model, the electronic eigenfrequencies have approximately the value of the energy difference between the centers of the valence and conduction bands, e.g., for the alkali halides about 10 eV. For the DSM, the eigenfrequencies of the "supershells" are about 1 eV, if again the shell mass is put equal to the free-electron mass. They are even lower if a higher mass is assumed in keeping with the fact that the narrow d bands



FIG. 9. Valence force-field parameter  $(\Delta\phi)(\Delta\phi')$  which yields the ratio  $A'_2/B'_2$  in agreement with the fit to experiment.



FIG. 10. Densities of states of the acoustic phonons for ZrC, NbC, and "NbN". The latter is assumed to have minimal frequencies near  $1 \times 10^{12} \text{ sec}^{-1}$ . The DSM parameters for "NbN" are given in Table III.

have rather high effective masses. Nevertheless, the phonon frequencies are one order of magnitude lower than the shell frequencies, so that de adiabatic approximation still may hold.

# **VII. CONCLUSIONS**

A shell model with a free-electron screening is used to describe the phonon dispersion curves of ZrC and HfC, and the over-all shapes of the phonon spectra of TaC and NbC. Good agreement with experiment is obtained. The model parameters clearly show that there is a strong covalent metal-nonmetal bonding and, to some extent, an ionic bonding with the carbon ion being negatively charged. The effect of metallic bonding is less important but not negligible. This result supports the "covalent-bonding" model, which is also confirmed by band-structure calculations. In contrast UC shows rather strong U-U force constants, while the U-C coupling parameters are comparatively weak. In addition, there is no indication of ionic interaction. For UC the "interstitial-allov" picture seems to be appropriate.

We find an increase of the ionic charge and of the polarizability in HfC and ZrC as compared to NbC and TaC, in accordance with experimental results, and the large decrease of  $\omega_{TO}$  in the IVB-IVA compounds can thus be explained.

The very-soft-phonon modes in some restricted parts of the acoustic branches of TaC and NbC are not related to the Kohn effect (see Sec. III for details). On the contrary, they are found to be connected with definite lattice vectors: The softmode regions form a cube in  $\vec{q}$  space which touches the *L* points of the Brillouin zone and is swollen on the {100} faces (see Fig. 1). The existence of this "resonance cube" indicates the importance of couplings between first and second neighbors in the metal sublattice. However, these couplings correspond to very-long-range interatomic forces and cannot be described in the shell model even by using ten additional parameters.

We found that the phonon anomalies are caused by the metallic *d*-electron band, which gets filled when going from HfC to TaC or from ZrC to NbC. We think that the electronic polarizability increases in a resonancelike manner in the vicinity of the surface of the cube, owing to strong shortrange correlations of the *d* charge density. This leads to the phonon softening.

Within the framework of the shell model, we describe this process by introducing a new electronic degree of freedom, a further shell at the metal ions, which represents this d charge density. Our results show that attractive short-range interactions between first- and second-nearest-neighboring supershells cause the very-long-range ion-ion forces which are connected with the soft modes. As was discussed in Sec. VI, the values of the force constants between neighboring supershells strongly indicate that the phonon softening is caused by d electrons of  $T_{2g}$  symmetry. This is also corroborated by band-structure calculations.

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#### APPENDIX

The force-constant matrix  $R_{ij}(\kappa\kappa'; \bar{q})$  may be written as

$$\underline{\mathbf{R}} = \begin{pmatrix} \underline{\mathbf{T}}(11) & -\underline{\mathbf{T}}(12) \\ -\underline{\mathbf{T}}(21) & \underline{\mathbf{T}}(22) \end{pmatrix} \,.$$

Here 1 and 2 refer to carbon and metal atoms, respectively. Including first, second, and fourth nearest neighbors, the matrices  $\underline{T}(\kappa\kappa')$  are given by

$$T_{ij}(12) = T_{ij}(21) = \delta_{ij}[A(12)\cos x + B(12)(\cos y + \cos z)],$$
  
$$T_{ii}(\kappa \kappa) = T_{ii}(12) |_{0}$$

$$+2C_1(\kappa\kappa)(1-\cos y\cos x)$$

 $+A_2(\kappa\kappa)(1-\cos 2x)+B_2(\kappa\kappa)(2-\cos 2y-\cos 2z)$ ,

 $T_{ij}(\kappa\kappa) = (1-\delta_{ij}) [A_1(\kappa\kappa) - B_1(\kappa\kappa)] \sin x \sin y \ ,$ 

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where we have put  $q_i r_0 = x$ , etc., A(12) and B(12)are the nearest-neighbor force constants between carbon and metal atoms. The matrix  $\mathbf{R}'$  in the DSM is obtained by replacing  $A_1(22)$ ,  $B_1(22)$ ,  $C_1(22)$ ,  $A_2(22)$ , and  $B_2(22)$  by the respective primed quantities in  $[T_{ij}(22) - T_{ij}(12)|_0]$ .

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