Resonant Electronic Polarization in the Lattice Dynamics of Transition-Metal Compounds

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We interpret the recently observed anomalies in the phonon spectra of some transition-metal compounds as resonances in the electronic polarization. These effects are described by a specific extension of the shell model. The possible connections of these anomalies to lattice instabilities and superconductivity are discussed.

Recently, inelastic neutron scattering data for HfC, TaC, and NbC have been reported by Smith and Gläser.[1,2] The overall shapes of the dispersion curves of these compounds are similar; there are, however, interesting anomalies in the spectra. In this Letter we try to explain the interatomic forces in these crystals on the basis of a phenomenological treatment.

Transition-metal compounds have an unusual combination of physical properties[3] which are explained with the help of energy-band calculations.[4-7] They show a strong metal-nonmetal covalent bonding confirmed by various experimental investigations,[8-10] while the metal-metal bonding[11,12] seems to be less important.

We propose a phonon model for these crystals consistent with their electronic properties. The strong covalent bonds are described by strong nearest-neighbor force constants. The large splitting of the optical branches at higher $\vec{q}$ values is explained by a negative static charge of the carbon atoms. At longer wavelengths a few conduction electrons, about 0.1 per unit cell, produce a screening[13,14] which removes the splitting. For calculations we have used a shell model[15,16] together with a generalized screening mechanism[14] leading to the following contribution of the dynamical matrix:

$$D_{\alpha\beta}{}^{\mathrm{sc}}(\kappa\kappa', \vec{q}) = 4\pi Z_A{}^{\kappa} Z_A{}^{\kappa'} \frac{q_\alpha q_\beta}{q^2}\left(\frac{1}{\epsilon(q)} - 1\right), \qquad (1)$$

with

$$\epsilon(q) = 1 + \frac{k_s{}^2}{q^2}\left(\frac{1}{2} + \frac{4k_{\mathrm{F}}{}^2 - q^2}{8k_{\mathrm{F}} q} \ln\left|\frac{2k_{\mathrm{F}} + q}{2k_{\mathrm{F}} - q}\right|\right). \qquad (2)$$

The charge Z_A has been determined by the condition $\omega_{\mathrm{LO}} = \omega_{\mathrm{TO}}$ at Γ. The model parameters have been determined by a least-squares fit (Table I).

TABLE I. Shell-model and screening parameters. The notation follows Ref. 17. The numbers 1 and 2 refer to C and Ta, respectively. The entries on the left-hand side are in units of $e^2/2r_0{}^3$.

$A(12) = 20.38$	$Z_1 = -Z_2 = -0.75e$
$B(12) = 6.39$	$Y_1 = 0$
$A(22) = 9.49$	$Y_2 = -1.52e$
$B(22) = -2.73$	
$k_1 = 228.5$	$k_s = 0.47(2\pi/2r_0)$
$k_2 = 184.4$	$k_{\mathrm{F}} = 0.37(2\pi/2r_0)$

We note that a shell model with neutral atoms gives very unsatisfactory results for higher $\vec{q}$ values.

The model describes quite well the overall shapes of the dispersion curves in HfC, TaC, and NbC. In addition, TaC and NbC show rather sharp minima mainly in the acoustic branches (Fig. 1). If the number of valence electrons (ve) is diminished from the value 9 (TaC, NbC) to about 8 (HfC,[7] $\mathrm{NbC}_{0.75}$[2]), these minima disappear without any shift of their positions. This contradicts the interpretation that the effect results from Kohn anomalies.[18] HfC shows a lowering of the optical frequencies near $\vec{q} = 0$ of about 25% which is not exhibited in $\mathrm{NbC}_{0.75}$.

For TaC and NbC, a phase analysis of the $\vec{q}$ values of the minima hints that these are determined by $q_\alpha \approx \pm\frac{1}{2}$, $\alpha = x, y, z$. This defines the surface of a cube which touches the first Brillouin zone at eight L points. In real space this means that there exists a strong coupling in every simple cubic metal sublattice. This coupling corresponds to very long-range interatomic forces[1,19] and cannot be described by using even ten additional parameters in the simple shell model. We think that the origin of these long-

TABLE II. ESM parameters for TaC and HfC (in units of $e^2/2r_0^3$). A^n, B^n, C^n denote the nth nn coupling constants in the metal sublattice. A is for radial B and C for tangential cc. A_{MC} and B_{MC} are corresponding radial and tangential nn metal-carbon cc.

TaC		HfC
$A^1=1.79$	$A^2=2.39$	$A_{MC}\approx 5.6$
$B^1=1.06$	$B^2=0.54$	$B_{MC}=1.0$
$C^1=0.0$	$A^3=0.30$	

range forces might be a strong short-range correlation in the electronic charge density. This leads to a $\vec{q}$-dependent polarizability of the metal ions which becomes resonant near $q_\alpha \approx \frac{1}{2}$ and could result in a singularity of the dielectric function. In HfC, the soft modes are the optical modes at Γ. It seems possible that an analogous correlation in the metal-carbon coupling is the origin of this effect.

In order to describe this resonant behavior we modify the shell model by introducing a coupling of the induced electronic polarization w at different ions via a short-range correlation field w_1. Our model has the matrix form

$$\begin{aligned} \mathfrak{M}\omega^2 u &= (R+ZCZ+D^{sc})u + (R+ZCY)w, \\ 0 &= (R+YCZ)u + (k_c+R+YCY)w + R_1 w_1 \\ &= R_1^{\dagger} w + k_1 w_1. \end{aligned} \tag{3}$$

The "correlation" matrix R_1 has the same structure as the usual force-constant matrix R.[17] The various coupling parameters are explained in Table II. In the diagonal matrix

$$k_1 = \begin{pmatrix} k_c & 0 \\ 0 & k_M \end{pmatrix},$$

which is analogous to k_0 in the shell model, we put $k_c^{-1}=0$ and normalize the redundant parameter $k_M = 1$. From (3) we derive the dynamical matrix

$$\begin{aligned} D &= R + ZCZ + D^{sc} \\ &\quad - (R+ZCY)[k(\vec{q}) + R + YCY]^{-1}(R+YCZ), \end{aligned} \tag{4}$$

with the $\vec{q}$-dependent polarization matrix

$$k(\vec{q}) = k_0 - R_1(k_1)^{-1}R_1^{\dagger}.$$

It is obvious that the new coupling does not affect

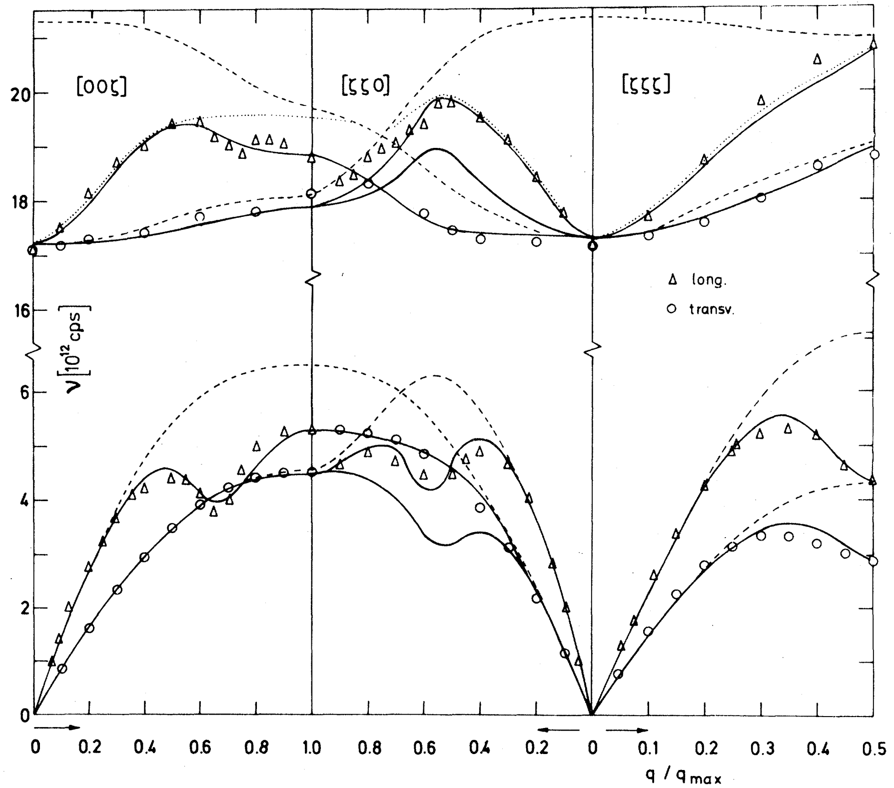

FIG. 1. Phonon dispersion curves for TaC. Triangles and circles, experimental values (Ref. 1); dashed, dotted, and solid lines show results obtained from simple shell model, simple shell model with screening, and ESM, respectively.

the elastic behavior.

We have calculated dispersion curves for HfC, and TaC, and preliminary curves for NbC. The results for TaC are shown in Fig. 1 for the simple shell model, the shell model with screening, and our extended shell model (ESM). The ESM predicts a minimum in the lower TA ($1\bar{1}0$) branch in the [110] direction. The parameters are fitted to experimental data by a least-squares technique (Table II). There remain small discrepancies between experiment and theory.

In the case of TaC all additional coupling constants (cc) of $\boldsymbol{R}_1$ describe correlations in the metal sublattice only. The main features of the anomalous behavior are described by the second-nearest-neighbor (nn) parameter A^2 which essentially produces the "resonance cube" in $\vec{q}$ space. The nn cc $\boldsymbol{A}^1$ and $\boldsymbol{B}^1$ influence the overall shape and shift the positions of some minima to slightly higher $\vec{q}$ values. C^1, which acts perpendicular to the xy plane, turns out to be nearly 0. This result corresponds to a deformation of electronic charge density with d_{xy} symmetry which excludes coupling perpendicular to the xy plane. Minor corrections are given by B^2 and A^3. For HfC, apart from a 20% reduction of k_s, we have used the unchanged parameters of the shell model for TaC given in Table I. Here, the metal-carbon cc A_{MC} and B_{MC} (Table II) of R_1, which correspond to metal-nonmetal correlations, describe the resonance at Γ. The results for the optical branches are shown in Fig. 2. For the acoustic branches we also get a good description.

In our treatment we discuss two different types of resonances. We suppose the first one, with $\vec{q} = 0$, to be related to the few unoccupied p-d bonding states in compounds with 8 ve such as HfC. This mechanism fades away in compounds with filled p-d bands such as TaC, NbC (9 ve), and, interestingly, in the nonstoichiometric $NbC_{0.75}$.[2] The stability of similar substances and the difficulty in building exactly stoichiometric compounds might be related to a tendency to avoid a filling of antibonding states.

The second mechanism, with $q_\alpha \approx \frac{1}{2}$, affects only the coupling in the metal sublattice of TaC and NbC, and parallels the filling of the new d band.[7] If we assume that the strength of the resonance effect is proportional to the number n_d of the additional d electrons, we obtain phonon instabilities at $q_\alpha \approx \frac{1}{2}$ for TaC for a critical value of $n_d = 9.5$ ve. In fact, a phase transition from the fcc to the hcp structure occurs in the system TaC_xN_{1-x} near $x = 0.4$ corresponding to 9.6 ve.[20] Similar structural changes in other transition-metal compounds may happen for the same reason. The mechanical behavior of transition-metal carbides is also consistent with this picture.[21]

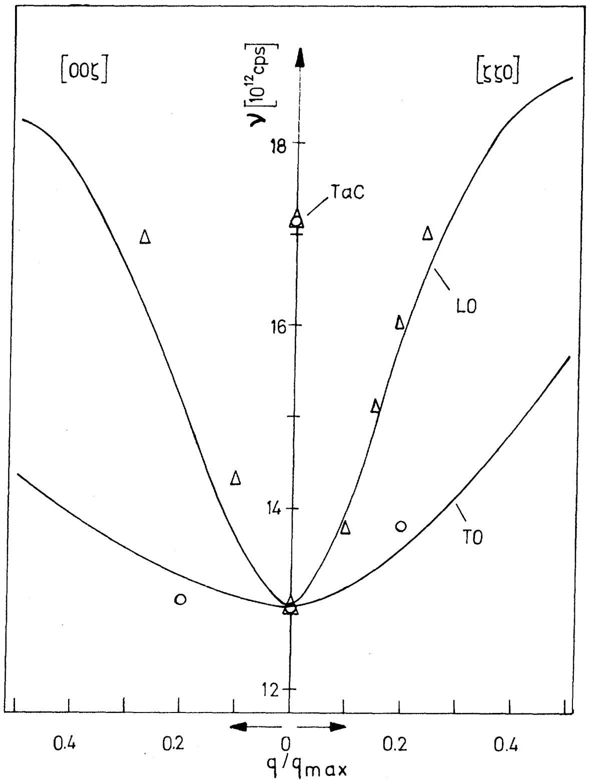

FIG. 2. Optical branches of HfC calculated with ESM. Experimental values are unpublished data by Smith and Gläser.

The resonant polarization discussed above might be related to the high superconducting transition temperatures T_c in TaC, NbC, etc. The possible effect of a short-wavelength polarizability of d electrons on T_c has been recently discussed by Matthias, Suhl, and Ting.[22] We think that our treatment strongly supports this general idea. In the light of the theories of McMillan[23] and Hopfield,[24] the importance of a strong increase in the moment $\langle\omega^{-2}\rangle$ of the phonon spectrum is obvious. Quantitative calculations of this effect are under way.

The connection between lattice instabilitities and high values of T_c in transition metals and their compounds has been emphasized by Phillips,[25] Fröhlich,[26] and Zeller.[27] Our treatment gives a description of the "over-screening"[25] process going on in these compounds. Anharmonic effects seem to be small for TaC and NbC, corresponding to the small temperature effects found by Smith and Gläser.[7] They might become more important in systems like $TaC_{1-x}N_x$ and NbN, which are nearer to the suggested phonon instabilities. Anharmonicity should in general tend to stabilize the phonons in the neighborhood of the critical $\vec{q}$ regime. Additional information obtained by measuring Grüneisen parameters, etc., would be helpful for a further analysis.

We think that our treatment may be useful for a microscopic analysis of the phonon self-energy. The inspection of phonon spectra of some transition metals like Nb,[18] as well as those of highly polarizable insulators, indicates that the idea of $\vec{q}$-dependent ion polarizabilities may be a helpful concept. These problems will be discussed in a forthcoming paper.

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[18] Note the analogous behavior of the Δ_1 (LA) branch in Nb-Mo alloys [B. M. Powell, P. Martel, and A. D. E. Woods, Phys. Rev. 171, 727 (1968)]. The pronounced minimum near $\zeta = (0, 0, 0.6)$ in Nb disappears when going to Mo *without any shift in* $\vec{q}$ *space.* The observed Kohn anomalies are much weaker and show a strong $\vec{q}$ dependency of their positions when changing the Mo concentration.

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