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Phonon anomalies in transition-metal nitrides: TiN

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For the first time we have observed soft-mode behavior in a superconducting transition-metal nitride. The phonon dispersion curves measured by inelastic neutron scattering exhibit sharp minima for the longitudinal-acoustic branches in the high-symmetry directions. The experimental results are well reproduced by calculations based on a double-shell model. The dispersion curves of TiN are similar to those of NbC except for significant difference in the anomalous region.

Transition-metal (TM) carbides and nitrides of group IV*b*, V*b*, and VI*b* form a class of materials with an unusual combination of physical properties. They combine extremely high melting points and hardness with metallic conductivity. Some of them are superconductors with transition temperatures up to $T_c \sim 18$ K. In recent years the lattice dynamics of carbides has been intensively studied both experimentally and theoretically. First measurements of phonon dispersion curves for carbides have been reported by Smith and Gläser.[1-3] They observed anomalies in the dispersion curves of the superconducting compounds NbC and TaC whereas no anomalies were found in the nonsuperconducting compounds ZrC and HfC. Theoretical investigations[4-7] starting from first principles have shown that both the phonon anomalies in the acoustical branches and the high superconducting temperatures originate from a resonancelike increase of the dielectric screening.

Up to now it has been an open question whether or not the *nitrides* of group IV*b* with nine valence electrons (VE) exhibit anomalies in the phonon dispersion curves like the isoelectronic group V*b* carbides. In this paper, we report for the first time on the phonon dispersion relations of a transition-metal nitride. Our measurements give conclusive evidence for the existence of pronounced phonon anomalies in these compounds.

Recently one of us (A.N.C.) has succeeded in growing single crystals of TiN sufficient in size and qualtiy for inelastic-neutron-scattering experiments. The sample was prepared by a zone-annealing technique.[8] A titanium rod was zone-annealed in a nitrogen-atmosphere of 99.9% purity under a pressure of ~2 MPa, at a temperature of 2600 °C, well below the melting point of TiN (2950 °C). The composition of the sample was determined by electron microprobe technique to be $TiN_{0.98}$. The mosaic spread of our sample was 0.3°.

Coherent-inelastic-neutron-scattering experiments were performed on the triple-axis spectrometers IN8 (acoustical branches) and IN1 (optical branches) at the HFBR in Grenoble. All measurements were made in the (110) plane of the sample. The results of our measurements are shown in Fig. 1. The most remarkable features in the dispersion relation are pronounced minima in the LA branches at reduced wave vectors $q \sim 0.65$ and $q \sim 0.55$ in the Δ and Σ directions, respectively, and at the L point. The TA branch at the L point appears only slightly depressed. In their overall shape the dispersion curves of TiN are

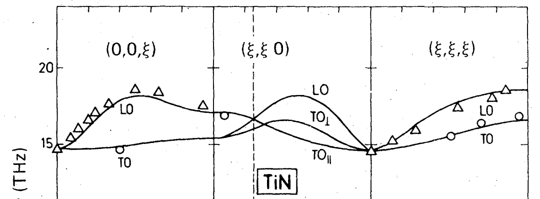

FIG. 1. Phonon dispersion curves for $TiN_{0.98}$ (Δ: longitudinal phonons, $\bigcirc$: transverse phonons). The full lines were calculated from a DSM fit; the broken lines describe the shell-model contribution.

TABLE I. Double-shell model parameters of TiN and NbC. Force constant in units of $e^2/2r_0^3$, screening vectors in units of π/r_0. The numbers 1 and 2 in parentheses refer to nonmetal and metal atoms, respectively The subscripts n refer to nth-order neighbors in the fcc metal sublattice. Primed force constants refer to the supershell.

	$A(12)$	$B(12)$	$A(22)$	$B(22)$	$C(22)$	$Z(1)$	$Y(1)$	$Y(2)$	$k(1)$	$k(2)$
TiN	18.53	1.92	11.65	−3.18	0.00	−0.70	0	0	∞	41.6
NbC	19.62	3.92	9.02	−0.70	−0.70	−0.696	0	−1.6	726	145

	k_F	k_S	A'_1	B'_1	C'_1	A'_2	B'_2	k'
TiN	0.3	0.3	−0.3987	−0.0942	−0.0428	−0.4112	0.0213	1.9
NbC	0.4	0.4	−0.713	−0.484	0.0	−0.943	−0.136	6.0

reminiscent of those of the nine VE carbides NbC and TaC.

We use a double-shell model (DSM) for the description of the measured dispersion curves. The DSM of Weber[9] is an extension of the simple shell model by an additional electronic degree of freedom which is represented by a supershell for the TM atom. This model describes very well the dispersion curves of the V*b* carbides. A fit of the DSM to our data of TiN is represented by the full curves in Fig. 1. The measured phonon dispersion curves including the anomalous regions are well reproduced. The parameters of the DSM fit are listed in Table I; for comparison the values for NbC (Ref. 9) are also given.

We observe that the dominant contribution to the total binding force comes from a strong covalent metal-nonmetal bond. The metal-metal bond is weaker but still important. The ionic charges are nearly equal in TiN and NbC. We have treated the nitrogen ion as rigid ($k=\infty$). Furthermore we have put the charge of the titanium shell equal to zero, because the screened dipole-dipole interaction does not contribute appreciably to the dynamical matrix. However, the mechanical (short range) polarizability of the titanium ion as determined by the core-shell coupling constant $k(2)$ turns out to be large for TiN. The subsets of parameters for TiN and NbC describing the simple shell model, show that ionicity and covalency are rather similar in both compounds, whereas the polarizability of the metal ion is strongly increased in TiN.

In Fig. 1 we show as broken lines the dispersion curves for TiN calculated from the simple shell model with the parameters given in Table I. A comparison with the full lines which are obtained by "switching on" the supershell interactions shows that contributions from the latter to the dynamical matrix are negligible outside a rather narrow region in q space. The shell-supershell coupling parameter k', which determines the width of the dips, turns out a factor of ~3 smaller in TiN than in NbC. This reflects the fact that the anomalies are more sharply defined in TiN than in NbC.

We note that there exists a qualitative difference between TiN and NbC concerning the contributions of supershell interactions to the dynamical matrix. In TiN, the LA branch in the vicinity of the X point is described well by the simple-shell-model contribution. This is in marked contrast to NbC and TaC (Ref. 9) where the nearest-neighbor supershell interaction lowers the LA frequency at the X point by about 20%. A similar situation exists for the acoustical branches in Λ direction. An analysis of the model shows that an increase of the polarizability of the Ti ions sharpens the resonance in the Λ direction and enhances the anomaly in the LA branch at the L point.

We have calculated the phonon distribution function of TiN from the DSM using a root sampling method due to Gilat and Raubenheimer.[10] In Fig. 2 our result for the acoustical part is compared

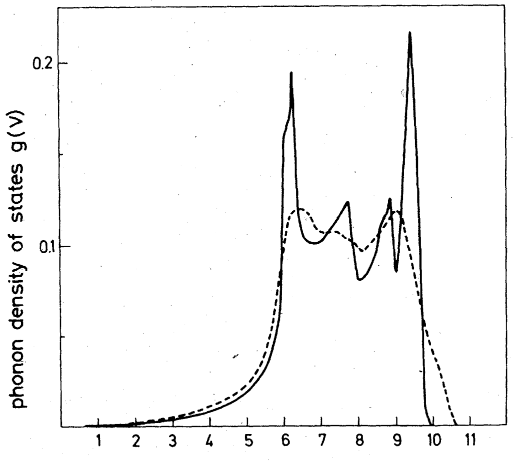

FIG. 2. Phonon frequency distribution function of acoustical phonons is calculated from the DSM using the parameters of Table I. The broken line shows experimental results for the phonon density-of-states of $TiN_{0.92}$ (Ref. 11).

with the phonon density-of-states determined by inelastic neutron scattering on $TiN_{0.92}$ powder[11] at room temperature. The experimental curve has not been corrected for instrument resolution. The measured cutoff frequency is slightly higher than the calculated one. This is due to the poorer stoichiometry of the sample used in the density-of-states measurement. Apart from this the agreement is satisfactory; in particular, the pronounced peaks in the theoretical curve are also found in the experimental density-of-states at the same phonon energies. Thus we conclude that our DSM calculations give a good description of the phonon dispersion not only in the high-symmetry directions, but over the whole Brillouin zone.

In conclusion, we found that TiN exhibits similar phonon dispersion relations as the isoelectronic group V*b* carbides. This is in accordance with a rigid-band picture which has been shown to be appropriate by band-structure calculations.[12-14] There exist, however, significant differences between carbides and nitrides. The phonon anomalies in TiN are confined to a narrower region in q space than in NbC and TaC and are less pronounced for the TA branches. These differences may become important in a trend analysis of the anomalies in carbides and nitrides based on microscopic theories. Our results give conclusive evidence that the excess density of states observed in measurements of the specific heat[15] and in the phonon density-of-states[16-18] is in fact due to soft mode regions in the phonon dispersion. A correlation has been established[4,7] between the evolution of phonon anomalies and the enhancement of superconductivity when going from eight VE to nine VE in TM carbides.

We conclude that a very similar correlation holds if the additional valence electron is provided by the nonmetal atom. Measurements of the phonon density-of-states[17,18] and of the specific heat[19] of the other group-IV*b* nitrides indicate that the lattice dynamics of these compounds is indeed very similar to that of TiN.

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