Phonon Anomalies in Transition-Metal Carbides*

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(Received 23 June 1972)

The phonon anomalies observed in superconducting TaC have been explained recently by Weber, Bilz, and Schröder with their *extended shell model*. Their model also predicts an anomaly in the transverse acoustic mode in the [110] direction with *xy* polarization—a branch which was not measured in the initial neutron investigation. The purpose of this Letter is to report the experimental confirmation of the Weber-Bilz-Schröder prediction, which gives added credence to their model, and to comment on the possible significance of these results.

In a recent Letter, Weber, Bilz, and Schröder[1] (WBS) reported lattice-dynamics calculations of the phonon frequencies in TaC and HfC. With their extended shell model (ESM) they were able to reproduce the phonon anomalies observed[2-4] in superconducting TaC for large wave vectors. The equations of motion [their Eq. (3)] contain terms that WBS interpret as a q-dependent polarizability of the metal ions, which exhibits resonance behavior in the vicinity of the anomalies; the large metal coupling constants, obtained as parameters from a least-squares fitting procedure, are attributed to a deformation of electronic charge density with d_{xy} symmetry.

Although the ESM model of WBS is phenomenological and the parameters are obtained by fitting to observed data, their calculations also predict an anomaly in the transverse acoustic mode in the [110] direction with xy polarization—a branch which was not measured in the initial neutron investigation. This is in marked contrast to the "normal" behavior observed (and calculated) for the transverse mode in this direction with z polarization. The difference in behavior of these two modes can be of great significance in choosing among various lattice dynamical models; therefore, it seemed highly desirable to check this prediction by additional neutron scattering measurements. The purpose of this Letter is to report a confirmation of the WBS prediction, which gives added credence to their model, and to comment on further neutron measurements of transition metal carbides as well as other models recently reported.

The experimental techniques have been reported previously[4] and will not be described here except to mention that the TaC single crystal used in the previous investigations was oriented for this study with a cube edge vertical and the scattering was observed in the ($hk0$) zone. This orientation permits the observation of the TA and LA modes in the [100] and [110] directions with polarization in the x-y plane, but precludes observation of modes with other polarizations and modes with directions out of the plane, such as the high-symmetry [111] direction.

The experimental points shown in Fig. 1 are the results of the phonon measurements by neutron scattering for the transverse acoustic modes in the [110] direction. The anomalous behavior of the $(TA)_{xy}$ is clearly indicated. Anomalous behavior in the corresponding optic branch was not apparent; however, further measurements and calculations are necessary and will be undertaken in the near future. The TA_{xy} mode anomaly has a frequency considerably below the corresponding

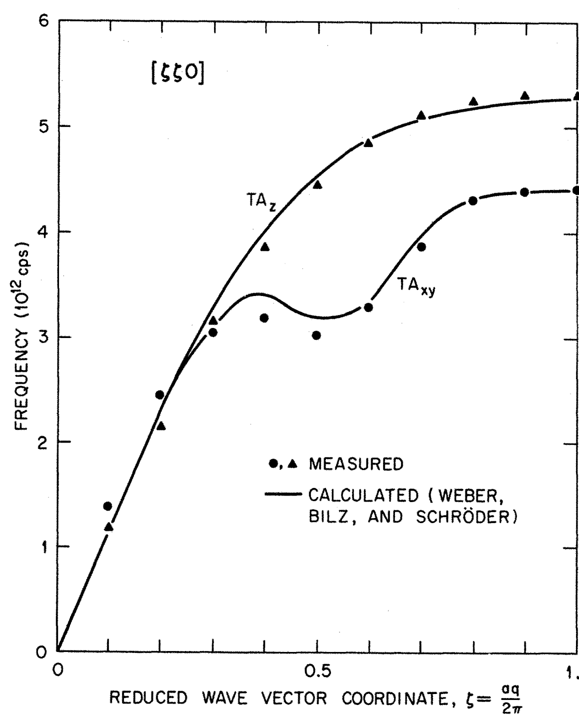

FIG. 1. Transverse acoustic modes in the [110] direction in TaC.

anomaly in the LA modes and if it goes softer, say, upon alloying with the nitride, where it has been shown that T_c increases with increasing x in $TaC_{1-x}N_x$ and $NbC_{1-x}N_x$, it could be the precursor of a lattice instability as discussed in more detail by Phillips[5,6] and Matthias.[7] This observation may have particular significance in relation to lattice instabilities in high-T_c superconductors and it may be more than just a coincidence that it is a similar mode which goes soft in high-T_c Nb_3Sn[8] and V_3Si.[9]

In another recent Letter, Ganguly and Wood[10] have suggested that the amonalous behavior of the LA [001] mode in bcc niobium may be associated with a frequency-dependent contribution to the dielectric response function. This contribution would arise from a small group of d electrons with low velocity at the Fermi surface which, in some cases, may also give rise to acoustical plasmons at low q values. This is an interesting possibility, but since it seems to imply the breakdown of the adiabatic approximation, it adds additional complexity to the lattice dynamical problem. Conceptually, the acoustic plasmon mechanism may be related to the resonant electronic polarization formalism of WBS; whereas the former implies the breakdown of the adiabatic approximation, it is not immediately obvious nor a necessary consequence that this is so for the latter model.

Because of the high neutron absorption and small crystal size the neutron measurements of the optic modes in HfC were very limited and subject to large experimental errors. However, in contrast to the modes in TaC, NbC, and even $NbC_{0.76}$, the modes exhibited a pronounced decrease in the degenerate TO and LO frequencies at $\vec{q}=0$, a feature also explained by the extended shell model of WBS. Recent measurements[11] of the phonon spectra in ZrC have confirmed this behavior in greater detail and with increased precision. This is also in marked contrast to the optic modes in metallic UC which are essentially flat.[12]

Further experimental and theoretical studies of high-temperature superconductors are needed and are, indeed, underway at several laboratories. At this laboratory neutron measurements of layer-type superconducting compounds and hcp metals are under investigation. It should be emphasized again that phonon anomalies of the type discussed here do not seem to be restricted to the transition metals with d electrons but have also been observed in several Pb alloys.[13] Hopefully, studies such as these and their successful theoretical interpretation will elucidate the nature of the electron-phonon interaction and the bonding properties in these materials.

The author is grateful to Professor H. Bilz and his colleagues for making their calculations available prior to publication and for interesting comments and discussions. He also wishes to thank R. F. Wood, B. N. Ganguly, M. Mostoller, and J. S. Faulkner for helpful discussions.

*Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

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