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Phonon Spectra in TaC and HfC†

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Phonon dispersion curves have been measured by one-phonon coherent inelastic neutron scattering in the high-symmetry directions of TaC at room temperature and at 4.2°K (superconducting transition temperature $T_c \approx 10°\mathrm{K}$). Pronounced structure is observed in the [001] and [110] directions for the longitudinal acoustic modes and, to some extent, for the longitudinal optic modes. By contrast, HfC ($T_c < 1°\mathrm{K}$) exhibits little or no structure in these modes.

Transition-metal carbides are intriguing compounds that are of interest for both fundamental and practical reasons. Not only do they have extremely high melting points and are very hard, but they exhibit metallic conductivity within the same order of magnitude as the metals themselves. In addition, many of them are superconductors with transition temperatures higher than the pure metals. Their superconducting properties are strongly dependent on the formal valence of the metal as well as the structure and stoichiometry of the crystals. McMillan[1] has emphasized the dependence of the electron-phonon coupling constant, and hence the superconducting transition temperature, on the phonon frequencies in strongly coupled superconducting metals. It is suggestive that these relations also apply to the transition-metal carbides.[2]

Rundle[3] regarded these compounds as electron-deficient structures, where the nonmetal atom forms more bonds than it has bond orbitals. He suggested strong metal-nonmetal directional bonds along with weaker metal-metal bonding to explain their conductivity, high melting points, and extreme hardness and stability. Bilz,[4] Ern and Switendick,[5] and Lye and Logothetis[6] have used a more formal band-structure approach in terms of molecular orbitals and have reached similar conclusions, although there is some disagreement in the interpretations of the relative strengths of the interatomic interactions.

A knowledge of the lattice dynamics of these compounds should help elucidate the various bonding mechanisms, such as relative strengths of metal-metal and metal-nonmetal bonding, degree and direction of charge transfer, and range of atomic interactions. Hopefully, information concerning the electron-phonon interaction and other properties related to superconductivity also may be deduced.

This communication reports preliminary results of a coherent inelastic neutron scattering study of the lattice dynamics of TaC and HfC in which unusual features are observed in the longitudinal modes in TaC (superconducting transition temperature $T_c \approx 10°\mathrm{K}$) but are not apparent in HfC (T_c, if it exists at all, $<1°\mathrm{K}$). Both compounds have the NaCl structure.

The phonon measurements were made on the automatic triple-axis neutron spectrometer[7] at the high-flux isotope reactor with variable incoming neutron energy E_0 and fixed outgoing energy E' in the neutron energy-loss mode of operation. Both "constant-$\vec{Q}$" and "constant-E" types of scans were made. The horizontal divergence of the entrance and exit soller-slit collimators was $\frac{2}{3}$° full width at half-maximum. A Be(101) plane was used as a monochromator, while both Be(002) and Ge(111) planes were used as analyzers. Throughout the experiment E' was set at 6.5×10^{12} cps.

The single crystals[8] were in the form of cylindrical rods 5-6 mm diam and of very good crystallographic quality (mosaic spread ≈0.1-0.2°). The TaC crystal was 33 mm long while the HfC crystal was only 22 mm long; both crystals were reported to be within 1% of stoichiometry. From our lattice-constant measurements at room temperature, $a_0(\mathrm{TaC}) = 4.4555$ and $a_0(\mathrm{HfC}) = 4.644$, and from previous studies[9,10] of the lattice-constant variation with metal/carbon ratio, we believe that the crystal of TaC does not deviate more than 1% from stoichiometry and that HfC is nearly stoichiometric. The crystals were rotated about the $[1\bar{1}0]$ axes and the measurements made in the [001], [110], and [111] directions. Typical phonon-scanning times for the TaC crystals were of the order of 1 to 2 h for the acoustic modes to several hours each for the optic modes. Because of the greater absorption cross section of Hf (104 b at $E' = 6.5\times10^{12}$ cps), the phonon measurements were much more difficult for HfC than for TaC; therefore, only a limited number of phonons were measured. It was particularly difficult to determine completely the shapes of the optic branches. Hopefully, larger crystals will become available.

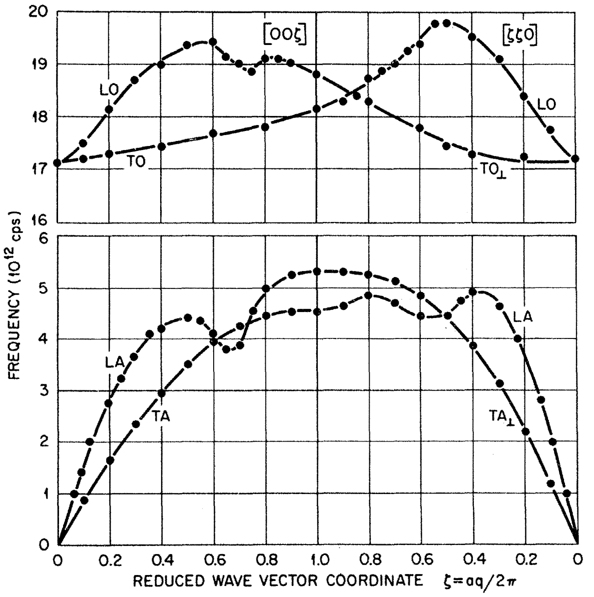

FIG. 1. Phonon dispersion curves for TaC at 298°K.

Figure 1 shows phonon dispersion curves in the [001] and [110] directions for TaC at room temperature. The slopes of the acoustic modes near $q = 0$ are, within experimental error, in agreement with those computed from the known elastic constants.[11,12] Figure 2 shows a comparison of the longitudinal acoustic modes for TaC and HfC. The most notable features are the oscillations in the longitudinal modes of TaC and the lack of such oscillations in the HfC curves (not unlike the observations for Nb [13] and Mo [14]). The structure is most pronounced for the acoustic modes, but still quite apparent in the optic modes. Less pronounced structure possibly exists in the HfC curves but higher resolution experiments will be necessary to reveal their details. A search for Kohn anomalies which may exist in TaC will also require studies with higher resolution.

Another prominent feature of the dispersion curves in Fig. 1 is the large gap between the acoustic and optic modes. Whereas in TaC the LO mode at $q = 0$ has a frequency $\nu = 17.2\times10^{12}$ cps, the corresponding mode frequency in HfC is only $\nu = 12.9\times10^{12}$ cps. The LO frequencies in HfC increase rather rapidly with increasing q and approach about the same maximum frequencies as in TaC. The large dispersion of the LO modes for small q, especially in HfC, possibly indicates strong screening effects of the nearby free electrons in the crystal.

The phonon dispersion curves measured in TaC at 4.2°K show the same overall behavior as the ones measured at room temperature except the structure in the longitudinal acoustic modes appears somewhat more pronounced. We were not able to detect any pronounced effect because of

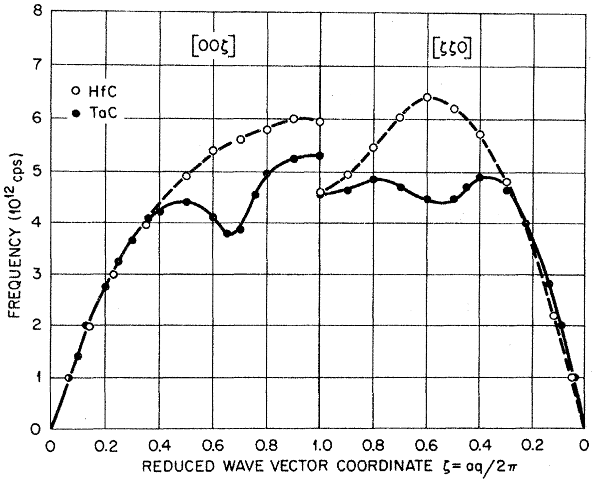

FIG. 2. Longitudinal acoustic modes in Ta and HfC.

the superconducting transition but this should be proved by very accurate measurements immediately below and above T_c.

In the first attempt to analyze the TaC room-temperature data, we have made a Fourier analysis of the sum of the squares of the optic and acoustic longitudinal frequencies for the [001] and [110] directions fitting expressions of the form[15]

$$\nu_{\mathrm{LO}}^2+\nu_{\mathrm{LA}}^2=\varphi_0+\sum_{n=1}^{N}\varphi_n(1-\cos n\pi q)$$

by a linear least-squares fit to the experimental data. The φ_n's can be interpreted in terms of interplanar force constants. In order to obtain reasonable agreement with the data at least ten planes had to be taken into account, which indicates a long range of the interatomic forces. Obviously, a simple lattice-dynamical model will not be able to explain the observed dispersion curves; nevertheless, a model based on Ta-C, Ta-Ta, and C-C short-range interactions only did approximately reproduce the observed frequencies (on the average within 10 to 15%) except in the regions of the oscillations. The resulting force constants representing the Ta-C interaction are large, and this fact, along with the large metal-to-carbon mass ratio, accounts for the observed wide gap between the acoustic and optic modes. However, the Ta-Ta force constants are only slightly smaller than the Ta-C force constants indicating appreciable metal-metal interactions. The C-C interactions are smaller but not negligible. Lattice-dynamical models which include long-range interactions and screening effects are under investigation and a more detailed study and analysis will be reported at a later date. This will include measurements in other directions in TaC as well as high resolution experiments immediately above and below the superconducting transition.

Because the only apparent difference between HfC and TaC is in the number of valence electrons (analogous to the difference in the electronic structure of Nb and Mo), the possibility the structure in the longitudinal modes is related to a large electron-phonon interaction is strongly suggested. This may be a reflection of the oscillations in the energy-wave-number characteristic, $F(Q)$, of Harrison[16] and would perhaps explain why the transverse modes in Fig. 1 are essentially unaffected, since $F(Q)$ does not contribute to these modes in the first Brillouin zone and is small for larger values of Q.

The studies will be extended to include the carbides of Zr, Nb, Ti, and V. Since the superconducting transition temperature[2,17] and other properties of TaC_x are strongly dependent on the carbon concentration it would be of great interest to measure the phonon spectra in nonstoichiometric single crystals if they become available.

It would be desirable, of course, to explicitly relate the observations reported here to the electronic properties of TaC and HfC but, unfortunately, little is known at present about the band structure and the Fermi surfaces of these compounds. Further experimental studies of the type described here undoubtedly will be of value in understanding the electronic and mechanical properties of the transition-metal carbides and related compounds.

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