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Direct Correlation of Phonon Anomalies in NbC with Fermi-Surface–Induced Maxima in Generalized Susceptibilities*

Michèle Gupta†
Magnetic Theory Group, Department of Physics, Northwestern University, Evanston, Illinois 60201
and
A. J. Freeman
Department of Physics, Northwestern University, Evanston, Illinois 60201, and Argonne National Laboratory, Argonne, Illinois 60439
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The generalized susceptibility of NbC, determined from its augmented plane wave energy band structure (with constant matrix elements), shows large maxima, arising in large part from Fermi surface "nesting," to occur at precisely those $\vec{q}$ values at which soft modes have been found in the phonon acoustic branches by Smith. These maxima can be represented by a warped cube of dimension $\sim 1.2(2\pi/a)$ in momentum space, in striking agreement with the soft mode surface proposed by Weber.

Long known for their remarkable properties such as high melting points and ultrahardness, the transition-metal carbides and nitrides are considered an important class of materials because of the occurrence of high superconducting transition temperatures, T_c. The systematic neutron-scattering determinations of phonon dispersion curves $\omega(\vec{q})$ in the carbides of the transition-metal IV and V series by Smith and Gläser[1] revealed the existence of soft phonons and led to attempts to correlate these soft-phonon modes to the high T_c values. Such a direct correlation between lattice instabilities and high T_c's is becoming more accepted; an important problem is the theoretical understanding of the origin of phonon-mode softening in superconductors. While rigorous formulations of dynamical matrix theory have been proposed, such as the work of Sinha,[2] based on the augmented plane-wave (APW) method, no *ab initio* calculational predictions of phonon spectra have been reported. A phenomenological model theory utilizing the modified shell and supershell model has been employed, particularly for NbC, by Weber, Bilz, and Schröder.[3] Weber[4] was able to show that the introduction of the supershell interactions, which describe the d-d metal interaction, is essential for obtaining the observed dips in $\omega(\vec{q})$. An important result was obtained by Mostoller[5] when he showed that the general shapes of the dispersion curves, but not the phonon anomalies, could be obtained using a free-electron dielectric screening function and describing the electron-ion interaction in a pseudopotential representation. More recently, Sinha and Harmon[6] were able to reproduce the longitudinal branches of the phonon dispersion curves in Nb and NbC by using a local pseudopotential to represent the electron-ion interaction. In this work, which necessarily introduced other approximations, the dielectric screening matrix was expressed in terms of several parameters which were determined by fitting the calculated longitudinal modes to the experimental values. While noting the possible importance of structure in the diagonal d-band part of the susceptibility function, Sinha and Harmon[6] assumed $\chi(\vec{q})$ to be $\vec{q}$ in-

dependent (and equal to the density of states at the Fermi energy) thereby assigning an important physical role to the high density of localized states (DOS) at the Fermi energy E_F and to the local field corrections.

In this Letter, we present the results of an accurate *ab initio* determination of the diagonal elements, $\chi(\vec{q})$, of the generalized susceptibility matrix for NbC and emphasize the very important role of structure in $\chi(\vec{q})$ for the occurrence of phonon anomalies. As is well known, $\chi(\vec{q})$ is related to the diagonal elements of the dielectric matrix by the relation $\epsilon(\vec{q},\vec{q}) = 1 + V(\vec{q})\chi(\vec{q})$, where $V(\vec{q})$ is the Fourier transform of the electron-electron interaction. We find that the calculated $\chi(\vec{q})$ shows a strong $\vec{q}$ dependence, contrary to what was previously assumed,[6] and maxima at just those $\vec{q}$ values at which the phonon dispersion shows soft modes to occur.

The energy band structure of NbC was determined from an *ab initio* APW calculation with an assumed lattice constant $a = 8.4472$ a.u. The warped muffin-tin crystal potential, obtained by superimposing the neutral-atom Hartree-Fock-Slater charge densities, was spherically averaged inside "muffin-tin" spheres of radii $R_{Nb} = 2.4596$ a.u., $R_C = 1.7333$ a.u.; the original Slater approximation, $\alpha = 1.0$, was used for the exchange potential. The APW basis set was expanded in a set of 68 plane waves and energy eigenvalues were obtained at 89 points of the $\frac{1}{48}$ irreducible Brillouin zone. The essential features of the band structure, to be described elsewhere, agree with the results obtained previously.[7] In agreement with the valence-band x-ray emission spectrum data of Ramqvist *et al.*,[8] we find a partial overlap of the Nb(4*d*) and C(2*p*) bands. After fitting of the band structure with a Fourier series (fifty symmetrized plane waves), the high-resolution density of states plotted in Fig. 1 was calculated using the analytic tetrahedron method of integration[9,10] in which the $\frac{1}{48}$ irreducible Brillouin zone was divided into 6144 tetrahedra. The Fermi energy ($E_F = 0.770$ Ry) lies at 0.052 Ry above the $\Gamma_{25'}$ state and falls in the "t_{2g}" band complex. In agreement with previous results, the DOS at E_F, 9.08 states/Ry·(unit cell), has essentially a 4*d* "t_{2g}" character with some C-2*p* hybridization.[7] The three bands which determine the Fermi surface (labeled as bands 4, 5, and 6—we omit the C-2*s* band) accommodate, respectively, 95.9%, 2.7%, and 1.4% of the remaining electron. Bands 5 and 6 both give rise to small electron surfaces around Γ, and have, respectively, the shape of a cube with stretched and rounded corners and of a rounded cube of dimension ~0.32 (in units $2\pi/a$). Band 4, which contains the majority of the electrons, gives rise to the multiply connected electron surface sketched in Fig. 2. Schematically, the six arms of the "jungle gym" around Γ can be considered as "flattened cylinders" whose cross sections perpendicular to the Γ-*X* directions can be characterized as "rounded squares" with dimensions which decrease from point *X* to Γ. The maxima of the flattened portions of the six arms are spanned at *X* by vectors belonging to the star $\vec{k} = \{0.7, 0.0, 0.0\}2\pi/a$.

The generalized susceptibility function, $\chi(\vec{q})$, which in linear response theory is the response

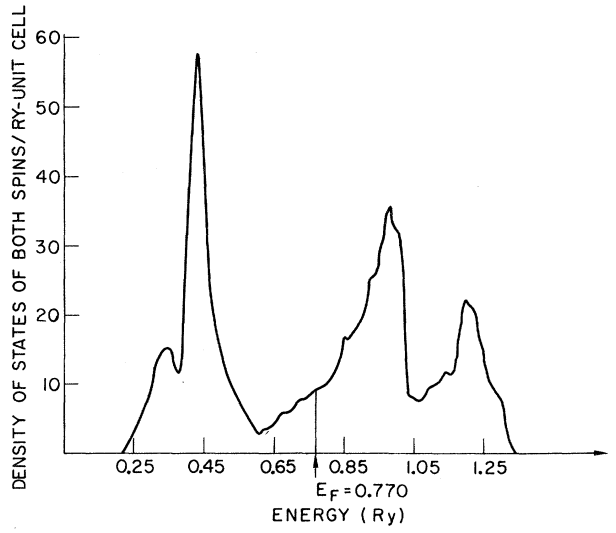

FIG. 1. Density of states of NbC (bands 1 to 8) where the zero of energy corresponds to the average potential outside the muffin-tin spheres.

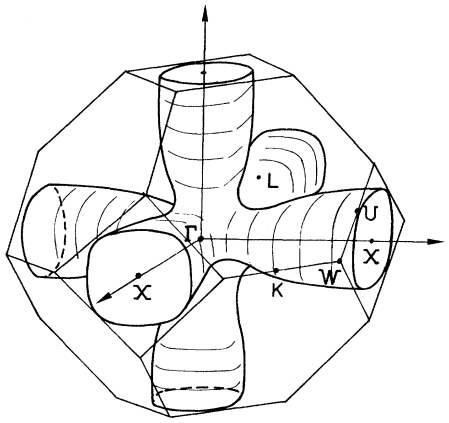

FIG. 2. The band-4 Fermi surface in the first Brillouin zone.

of the system to an external perturbation, plays an important role in the onset of spin-density waves, charge-density waves, and crystallographic phase transformations.[11] Without going through the exact derivation of the dynamical matrix, we note that divergences in $\chi(\vec{q})$ are related to a strong screening of the motion of the ions by the electrons; the ion-ion interaction is expected to be strongly modified by an anomalous response of the electrons and the phonon modes may be softened at those $\vec{q}$ values where the susceptibility function shows an anomalous behavior. From its energy denominator dependence, large contributions to $\chi(\vec{q})$ are expected when large portions of the Fermi surface (FS) are spanned by a given wave vector $\vec{q}$ ("nesting") or from parallel bands spanned by a $\vec{q}$ vector (so-called "volume effects").

We have calculated $\chi(\vec{q})$, at twenty equally spaced $\vec{q}$ points for each of the directions plotted in Fig. 3. In addition, the mesh around each of the maxima was further decreased in order to define better the peaks shown. We used the accurate analytic tetrahedron integration method of Rath and Freeman[10] with 2048 tetrahedra in the $\frac{1}{48}$ irreducible Brillouin zone. The most remarkable feature is the presence of maxima in the intraband contribution of band 4 to $\chi(\vec{q})$ at $\vec{q}=(0.6, 0.0, 0.0)$, $\vec{q}=(0.55, 0.55, 0.0)$, and $\vec{q}=(0.5, 0.5, 0.5)$ in units of $2\pi/a$ which precisely match the positions of the soft phonon modes measured by Smith.[1] The calculated peaks are broad, as are the dips in the dispersion curves. Both "nesting" (Fermi surface) and volume (band) effects contribute to the position of the maxima singled out in the $\chi(\vec{q})$ calculations especially in the [111] direction where FS "nesting" gives a range of possible q_{max} values. For the [100], [110], and [111] directions, the maximum in $\chi(\vec{q})$ is, respectively, 33.3%, 55.2%, and 91.7% higher than the value of the function at $\vec{q}=0$ (which is the contribution of band 4 to the DOS at E_F). A striking feature of these results, emphasized by Weber, is that the ratios of these maxima also match closely to the magnitude of the depth of the mode softening as can be seen by calculating $\omega^2(\mathrm{ZrC})-\omega^2(\mathrm{NbC})$ at the $\vec{q}$ values where anomalies occur for NbC (note that ZrC does not possess any phonon anomalies). The small intraband contribution from bands 5 and 6 shows "step"-like functions, as is expected from the shape of the Fermi surfaces of bands 5 and 6. For completeness we show the total interband contribution to $\chi(\vec{q})$ at the top of Fig. 3.

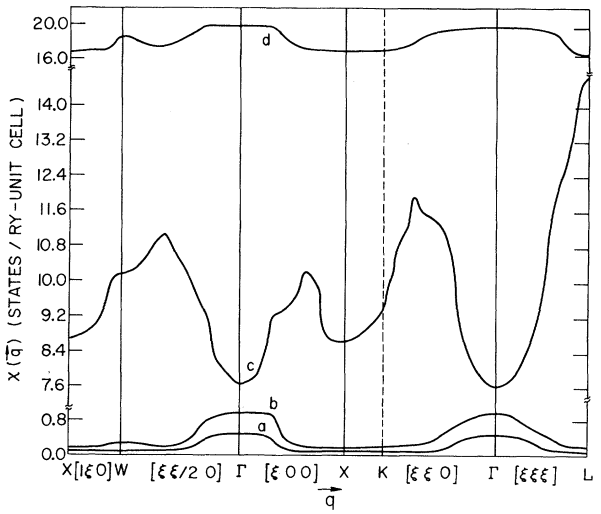

FIG. 3. The generalized susceptibility function $\chi(\vec{q})$ along several symmetry and off-symmetry directions: *a*, the intraband contribution from band 6; *b*, the intraband contribution from band 5; *c*, the intraband contribution from band 4; and *d*, the total interband contribution from bands 4, 5, 6.

We have also investigated off-symmetry directions such as the $[\xi, \xi/2, 0]$ (Γ to W) direction where a maximum in the intraband contribution to $\chi(\vec{q})$ from band 4 was found for $\xi=0.65$. In fact, the locus of the calculated maxima of the generalized susceptibility function appears to be a surface which can be represented schematically as a warped cube of dimension $\sim 1.2\times 2\pi/a$ in momentum space, centered at Γ. This result is in striking agreement with the soft-mode surface proposed by Weber[4] on the basis of a resonance increase of the electronic polarizability for metal nearest neighbors vibrating in phase opposition.

The possibly important role played by the matrix elements (ME) has been stressed by several authors[12-14] for several transition metals: Gupta and Sinha[12] (for Cr) and Gupta and Freeman[14] (for Sc) make an explicit use of the APW Bloch functions while Cooke, Davis, and Mostoller[13] (for Nb) calculate the matrix elements in the tight-binding approximation. Since matrix elements were not included in this work, we separated the interband from the intraband contributions in order to obtain a better understanding of their relative importance. As is clear from Fig. 3, the interband value (without ME) provides a large background for all $\vec{q}$ values, ranging from ~ 16 to 20 states/Ry·(unit cell); this is about 2 times larger than the DOS at E_F. It is well known

that the large value of the interband contribution at $\vec{q}=0$ is zero when ME are included. Moreover, from all previously reported results with nonconstant ME,[12-14] it is seen that the background is largely suppressed for *all* $\vec{q}$ values. [For example, whereas $\chi(\vec{q})$ without ME in Cr ranges from 132 to 140 states/Ry·atom, it never exceeds 9 states/Ry·atom when the ME are included (because of a drastic reduction of the interband value) and so the variation of $\chi(\vec{q})$ (about 8 states/Ry·atom) remains unaffected by the inclusion of ME. Similarly, $\chi(\vec{q})$ without ME for Nb varies between ~60 to ~68 states/atom ·Ry·spin in the ΓH direction while the result with ME varies between ~11 (at $q=0$) to 3.8 states/atom·Ry·spin at H.]

For this reason, and because the interband contribution without ME is remarkably structureless, we do not expect the interband part with ME to give rise to sharp structure. On the other hand, the inclusion of ME into the intraband contribution would modify the results shown in Fig. 3 by only a slowly varying function (essentially the square of the form factor). But if we recall the large heights of the peaks emphasized earlier, it seems very improbable that the ME could smear out the strong structure observed without ME and so we do not expect our general conclusions to be severely affected.

Calculations carried out for TaC also show maxima in $\chi(\vec{q})$ at those $\vec{q}$ values for which soft modes have been observed.[1] Surprisingly, we find that even the small shift in the q value at which the anomaly occurs in the [100] direction in going from NbC to TaC ($q_{\text{th}}=0.60$ vs 0.63) reproduces the trend in the shift observed experimentally ($q_{\text{exp}}=0.60$ vs 0.65). Finally, using our results for NbC and a rigid band model, we may understand qualitatively why no phonon anomalies are observed in the phonon spectrum of ZrC. The Fermi energy falls at the minimum of the DOS curve shown in Fig. 1 and the Fermi surface no longer possesses the nesting features seen for NbC (and TaC) and, hence, no maxima in $\chi(\vec{q})$ are expected. Keeping in mind the limitations of the rigid-band model, the general trend derived from our calculation agrees with experimental observations and appears to be consistent with the role of the electronic response function in the occurrence of phonon mode softening.

We have found that the structure of the $\chi(\vec{q})$ function correlates directly with all observed phonon anomalies in NbC (and TaC) and should be included in all *ab initio* calculations of the phonon dispersion curves. It would be of great interest for the understanding of the origin of phonon mode softening to examine whether the conclusions reached for NbC can also be applied to other carbides and nitrides of the transition-metal IV and V series; such a study is now in progress.

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†On leave from Le Centre de Mécanique Ondulatoire Appliquée du Centre National de la Recherche Scientifique, 23, rue du Maroc, 75019 Paris, France.

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