[5]V. Yakhot, M. Berkowitz, and R. B. Gerber, Chem. Phys. 10, 61 (1975).
[6]V. E. Bondybey and L. E. Brus, J. Chem. Phys. 63, 794 (1975).
[7]V. E. Bondybey, J. Chem. Phys. 65, 5138 (1976).
[8]L. Abouaf-Marguin, B. Gauthier-Roy, and F. Legay, to be published.
[9]M. Berkowitz and R. B. Gerber, to be published.
[10]W. Nielson and R. B. Gordon, J. Chem. Phys. 58, 4149 (1973).
[11]A. Maradudin, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1966), Vol. 18, p. 273.
[12]L. E. Brus and V. E. Bondybey, J. Chem. Phys. 63, 786 (1975).
[13]K. F. Freed and H. Meitiu, Chem. Phys. Lett. 48, 262 (1977).
[14]R. B. Gerber and M. Berkowitz, to be published.

Electron-Phonon Contribution to the Phonon Linewidth in Nb: Theory and Experiment

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We present theoretical calculations and experimental measurements of the phonon linewidth for Nb. The calculations employ the rigid muffin-tin approximation and a realistic band structure. The measurements were done at low temperature to minimize the contributions to the linewidth from phonon-phonon interactions. The calculations predict and experiments confirm strong electron-phonon coupling for the longitudinal phonon modes in the [110] direction.

The phonon linewidth contains very detailed information concerning the electron-phonon interaction. Allen[1] has shown that the electron-phonon contribution to the linewidth of a phonon having mode index i and crystal momentum $\vec{q}$, $\gamma_i(\vec{q})$, measures directly the contribution to the total phonon-mediated electron-electron coupling arising from this particular phonon. Thus the electron-phonon coupling parameter λ which determines the electronic mass enhancement and superconducting transition temperature[2] is simply a weighted average of the phonon linewidth,

$$\lambda = \sum_{\vec{q},i} \gamma_i(\vec{q})/\pi N(E_F)\omega_i^2(\vec{q}),$$

where $N(E_F)$ is the density of states of one spin at the Fermi energy.[3] The spectral function[4] $\alpha^2(\omega)F(\omega)$, obtainable from tunneling measurements, may also be written as an average over the linewidth as

$$\alpha^2(\omega)F(\omega) = \sum_{\vec{q},i} \gamma_i(\vec{q})\delta[\omega - \omega_i(\vec{q})]/2\pi N(E_F)\omega. \quad (1)$$

Linewidth measurements are very important for Nb because Nb has the highest transition temperature of any element and because the tunneling measurements on Nb remain quite controversial.[5,6] Axe and Shirane,[7] Shapiro, Shirane, and Axe,[8] and Bobrovskii *et al.*[9] have measured phonon linewidths in Nb_3Sn, Nb, and Pb, respectively. These Nb and Nb_3Sn measurements were, however, limited to transverse modes and to frequencies less than twice the superconducting energy gap.

The linewidth can be calculated as a double Fermi-surface integral

$$\gamma_i(\vec{q}) = (\pi\hbar/2M_a)\sum_{\vec{k},\vec{k}'} \delta(E_{\vec{k}} - E_F)\delta(E_{\vec{k}'} - E_F) \times \delta(\vec{k} - \vec{k}' - \vec{q})|M_{\vec{k},\vec{k}'}^i|^2, \quad (2)$$

where M_a is the atomic mass. The matrix element $M_{\vec{k},\vec{k}'}^i$ is given by $M_{\vec{k},\vec{k}'}^i = \int d^3r\, \psi_{\vec{k}}^*(\vec{r})\epsilon_{\vec{k},\vec{k}'}^i \times \nabla V \psi_{\vec{k}'}(\vec{r})$, where $\psi_{\vec{k}}$ is an electronic wave function, ϵ is a phonon polarization vector, and ∇V represents the change in crystal potential due to the displacement of a single atom. In our calculations we have employed the rigid muffin-tin approximation[10] which has been applied to a number of systems[11,12] and which seems to predict the correct magnitude and trends for the average electron-phonon coupling strength in the transition metals.[13]

We have calculated $\gamma_i(\vec{q})$ throughout the Brillouin zone by performing the integrations indicated in Eq. (2). Each Fermi-surface integration extended over a mesh of 53424 first-principles points at the Fermi energy. Values of $\gamma_i(\vec{q})$ were stored in 5200 bins chosen to fill the irreducible wedge of the phonon Brillouin zone. The results of our calculations (described below) indicated considerable variation in $\gamma_i(\vec{q})$ as a function of

both $\vec{q}$ and i. Since particularly large linewidths were predicted for the longitudinal modes in the [110] direction, we undertook a preliminary inelastic neutron scattering investigation of the phonon linewidths in Nb with primary emphasis on this direction.

The phonon linewidth measurements were made on the HB-3 spectrometer at the Oak Ridge high-flux isotope reactor under conditions of constant Q and constant E'; a value of $E' = 5.0$ THz was utilized for the latter throughout the investigation. The horizontal soller slit collimation was $\frac{1}{6}°$ before the sample and $\frac{1}{3}°$ after the sample. The monochromator was a Be(002) plane with a mosaic spread of 0.3° and the analyzer was either a Be(002) plane with a mosaic of 0.3° or a Be(101) plane with a mosaic of 0.1°. The Nb sample was a single crystal 4.5 cm long and 1.5 cm in diameter with an anisotropic mosaic spread which varied between 0.15° for the (002) reflection and 0.4° for the (220) reflection. The sample was mounted with the [1$\bar{1}$0] axis vertical in an Air Products closed-cycle He refrigerator and maintained at ≈ 13°K. About 45 phonon groups were measured at this temperature; however, a few measurements were made at room temperature for comparisons.

The instrumental contribution to the observed linewidths was calculated with the aid of the Cooper-Nathans resolution function[14] assuming a planar region of the dispersion surface in the vicinity of each wave vector measured. With the tight collimation used in the experiment the instrumental-resolution function is expected to be of Gaussian form if the sample mosaic is small and isotropic. For some of the narrow and well-focused transverse phonons somewhat asymmetric peak shapes were observed which are undoubtedly associated with the poor mosaic mentioned above; however, this anisotropy is not expected to affect greatly the longitudinal widths—at least those that are not sharply focused.

With only a few exceptions the observed widths are greater than the calculated instrumental widths. For the longitudinal modes in the [110] direction the measured widths greatly exceed the instrumental widths. In order to extract the non-instrumental contributions, the observed linewidths were assumed to be a convolution of a Gaussian width due to the instrumental contribution plus a Lorentzian width from electron-phonon and phonon-phonon contributions[15]; however, the phonon-phonon contributions are expected to be minimal at the low temperatures employed and the few phonon measurements at room temperature support this assumption.

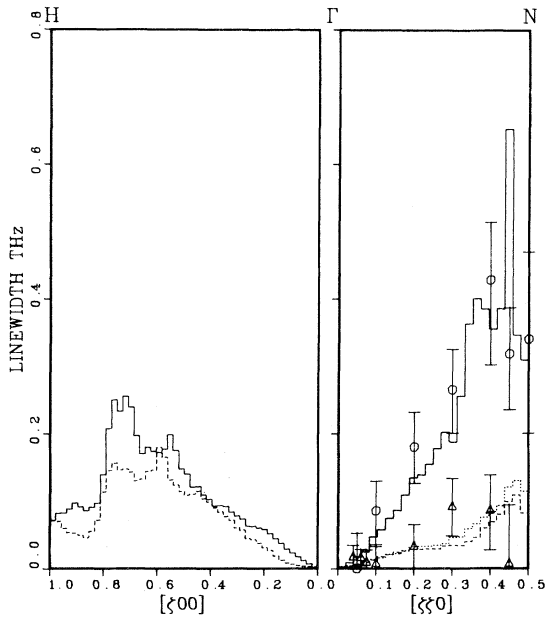

FIG. 1. Phonon linewidths in Nb. Histograms indicate calculated linewidths (full width at half-maximum). Solid histograms indicate longitudinal modes. Dashed and dotted histograms indicate transverse modes. Circles (triangles) are experimental longitudinal-(transverse-) mode linewidths. Measured transverse modes have [001] polarization.

Theoretically predicted linewidths are shown in Fig. 1 for the [100] and [110] symmetry directions. Experimentally determined linewidths for the [110] direction are also shown. The most apparent structure lies in the [110] direction where the longitudinal-mode linewidths are quite large and the transverse-mode linewidths small. Theory and experiment seem to be in reasonable agreement in this direction. The structure in this direction arises (according to the calculations) from the superposition of several peaks whose exact positions depend on the details of the Fermi-surface geometry so it is not surprising that the agreement is not perfect. The strong electron-phonon coupling for [110] longitudinal phonons arises mainly from scattering between states on the Fermi surface which lie near the line Σ (i.e., along [110]) in the electronic Brillouin zone. We shall show in a subsequent publication that the scattering rate for this type of scattering is enhanced by the phase relationships of the wave functions which enter the electron-phonon matrix elements.

A second interesting feature of the calculated

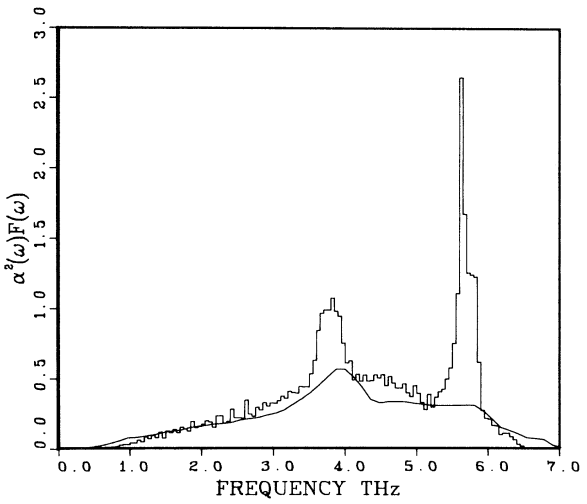

FIG. 2. Calculated and experimental spectral functions for Nb. The calculated spectral function should be broadened somewhat since the δ function in Eq. (1) should really be a Lorentzian of half-width $\gamma_i(\vec{q})$.

linewidths is the peak in the longitudinal mode for $\vec{q}=[0.73(2\pi/a),0,0]$. This peak arises from transitions between states in the ΓNH plane on the arms of the jungle-gym sheet. Unfortunately, the longitudinal- and transverse-phonon frequencies are degenerate at this point; so it is very difficult to unambiguously disentangle the linewidths experimentally.

The calculations generally predict somewhat larger linewidths for the longitudinal modes than for the transverse. This seems to be confirmed by the measurements made to date, although the extreme difference between longitudinal and transverse linewidths observed along [110] is probably atypical. In Fig. 2 we plot α^2F as calculated from the theoretical linewidths using Eq. (1). Also shown in an experimental spectral function from superconducting tunneling.[16] The calculated coupling is definitely stronger for the upper peak than is observed experimentally. At very low frequencies, on the other hand, the calculated α^2F lies substantially below the experimental. $\alpha^2(\omega)$ as obtained from the calculations is reasonably constant and equal approximately to 3 meV except for frequencies above 6.2 THz and below 1.5 THz in both of which cases it drops off precipitously. The calculated value of λ is 1.20 which is somewhat higher than the empirical estimate[13] of 0.97.

The theoretical prediction and experimental confirmation of strong electron-phonon coupling for phonons in the region of the Brillouin zone near the N point is particularly interesting because strong electron-phonon coupling is generally expected to be associated with anomalously soft phonons and this particular region has not previously been considered to be anomalous. An examination of the phonon dispersion curves for Nb-Mo alloys,[17] however, shows that the longitudinal-phonon frequencies along $[\zeta,\zeta,0]$ for $\zeta>0.3$ are strongly depressed in Nb relative to alloys containing 15% or 35% Mo. It is likely that addition of Mo to Nb decreases the electron-phonon interaction due to the reduction in $N(E_F)$ and allows the observed frequencies to rise toward their "bare" or unrenormalized values. It is significant that the transverse modes near the N point do not seem to be greatly affected by the addition of Mo which is consistent with our prediction and observation of rather weak electron-phonon coupling for these modes.

The most discussed anomaly in Nb is a dip in the longitudinal branch near $\vec{q}=[0.7(2\pi/a),0,0]$. Several apparently different explanations have been offered for transition-metal phonon anomalies including band-structure effects,[18] charge-fluctuation interactions,[19-21] and resonance screening effects,[22] but it is not clear to us whether or not these explanations are inconsistent with each other. We believe that band-structure effects are at least partially responsible for this anomaly since it coincides with a peak in the calculated linewidth. Pickett and Allen[23] have recently obtained a simple, approximate, semiempirical relation between the linewidth and the phonon-frequency renormalization, $\Omega_i^2(\vec{q})-\omega_i^2(\vec{q})=4\bar{\omega}\times\gamma_i(\vec{q})/\pi$, where Ω_i is a "bare" phonon frequency, ω_i is the observed phonon frequency, and $\bar{\omega}$ is a constant equal to 0.3 eV for the [100] direction in Nb. Applying this equation to calculate $\Omega_i(\vec{q})$ using our calculated values for $\gamma_i(\vec{q})$ removes most of the dip in the [100] LA branch and eliminates the nonlinearity of the [100] TA branch at low q. The Pickett-Allen formula can only be valid in some average sense, however, since $\gamma_i(\vec{q})$ can have discontinuities that are not expected to appear in $\omega_i(\vec{q})$.

Our results are relevant to the recent controversy over superconducting tunneling experiments on Nb and to the question of the possible failure of strong-coupling theory for this material.[5,6] The basic problem is that the tunneling experiments show substantially weaker coupling, especially at higher frequencies, than is consistent with the observed value of T_c and a reasonable value of the repulsive Coulomb pseudopoten-

tial, μ^*. We suggest that the tunneling experiments may not be picking up the full bulk electron-phonon coupling especially at the higher frequencies. In support of this suggestion we note that the area under the experimental $\alpha^2(\omega)F(\omega)$ curve, for frequencies greater than 5 THz, is less by a factor of 2.3 than the corresponding area under the calculated curve.[24] In addition, the calculated values of $\alpha^2(\omega)$ are supported by the admittedly limited linewidth data available at present. We also note that the electronic transitions contributing to the upper peak in $\alpha^2(\omega)F(\omega)$ occur primarily between states of unusually low Fermi velocity. This fact coupled with a relatively short lifetime for these states could lead to a very short mean free path *for those electronic states responsible for the high-frequency electron-phonon coupling.* Such a short mean free path (we estimate a few tens of angstroms) would make it questionable whether or not the effects of the coupling contributed by these states would appear in the tunneling current. More precise calculations of mean free paths and more extensive linewidth measurements are needed to test this suggestion.

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[1]P. B. Allen, Phys. Rev. B 6, 2577 (1972).

[2]W. L. McMillan, Phys. Rev. 167, 331 (1968).

[3]P. B. Allen (private communication) has pointed out a factor-of-2 error in Ref. 1.

[4]W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Chap. 11, p. 561.

[5]J. Bostock, V. Diadiuk, W. N. Cheung, K. H. Lo, R. M. Rose, and M. L. A. MacVicar, Phys. Rev. Lett. 36, 603 (1976); J. Bostock, K. H. Lo, W. N. Cheung, V. Diadiuk, and M. L. A. MacVicar, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass (Plenum, New York, 1976).

[6]B. Robinson, T. H. Geballe, and J. M. Rowell, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass (Plenum, New York, 1976).

[7]J. D. Axe and G. Shirane, Phys. Rev. Lett. 30, 214 (1973), and Phys. Rev. B 8, 1965 (1973).

[8]S. M. Shapiro, G. Shirane, and J. D. Axe, Phys. Rev. B 12, 4899 (1975).

[9]V. I. Bobrovskii, B. N. Goshehitskii, A. V. Mirmelshtein, and Yu. N. Mikhailo, Zh. Eksp. Teor. Fiz. 70, 1820 (1976) [Sov. Phys. JETP 43, 947 (1976)].

[10]G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. 28, 801 (1972).

[11]B. M. Klein, D. A. Papaconstantopoulos, and L. L. Boyer, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass (Plenum, New York, 1976).

[12]D. A. Papaconstantopoulos, L. L. Boyer, B. M. Klein, A. R. Williams, V. L. Morruzzi, and J. F. Janak, Phys. Rev. B 15, 4221 (1977).

[13]W. H. Butler, Phys. Rev. B 15, 5267 (1977).

[14]M. J. Cooper and R. Nathans, Acta Crystallogr. 23, 357 (1967).

[15]D. W. Posener, Aust. J. Phys. 12, 184 (1959).

[16]J. M. Rowell and B. Robinson, private communication; see also Refs. 5 and 6. The spectral function of Bostock *et al.* differs primarily in showing weaker coupling at lower frequencies.

[17]B. M. Powell, P. Martel, and A. D. B. Woods, Phys. Rev. 171, 127 (1968).

[18]S. T. Chui, Phys. Rev. B 9, 3300 (1974).

[19]N. Wakabayashi, to be published.

[20]P. B. Allen, Phys. Rev. B, to be published.

[21]S. K. Sinha and B. N. Harmon, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass (Plenum, New York, 1976).

[22]W. Hanke, J. Hafner, and H. Bilz, Phys. Rev. Lett. 37, 1560 (1976).

[23]W. E. Pickett and P. B. Allen, Phys. Rev. B (to be published).

[24]Very recent calculations of $\alpha^2(\omega)F(\omega)$ for Nb by B. N. Harmon and S. K. Sinha [Phys. Rev. B (to be published)] and by C. M. Varma and W. Weber (private communication) seem to be in general agreement with ours especially as to the existence of stronger electron-phonon coupling above 5 THz than has been observed experimentally.