Electron band structure, resistivity, and the electron-phonon interaction for niobium under pressure

J. Neve
Department of Theoretical Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

B. Sundqvist
Department of Physics, Umeå University, S-901 87 Umeå, Sweden

Ö. Rapp
Department of Solid State Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden
(Received 2 March 1983)

Accurate measurements of the electrical resistance of Nb are presented as a function of temperature and pressure in the region 0—40 °C and 0—1 GPa. From these measurements and published results for the compressibility and the pressure dependence of the superconducting transition temperature T_c we evaluate the pressure dependence of the electron-gas plasma frequency $\omega(p)$. The electronic structure of Nb is calculated from a self-consistent linear muffin-tin orbital method and results are obtained for the pressure dependence of the density of states at the Fermi surface, the root mean square over the Fermi surface of the Fermi velocity, the optical mass, and the plasma frequency. The experimental and calculated results for the pressure dependence of $\omega(p)$ are both close to $d\ln\omega^2/d\ln V = -1.9$. This agreement suggests that measurements of the electrical resistance as a function of temperature and pressure provide a new test of band-structure calculations. From our measurements of the resistance and calculations of $\omega(p)$ and from published results for the compressibility we obtain the pressure dependence of the electron-phonon interaction $\lambda(p)$. With p given in gigapascals, the result is $d\ln\lambda/dp = -0.0047$.

I. INTRODUCTION

Experimental techniques to study the pressure dependence of average electron band-structure properties have usually focused on results for the density of states $N(E)$. Several examples are[1] the pressure dependence of the Pauli spin paramagnetism, the low-temperature thermal expansion, tunneling experiments on superconductors under pressure, and indirect information from the pressure dependence of the superconducting transition temperature $T_c(p)$.

Apart from the limited accuracy of some of these methods, the comparison with theoretical results is also impeded by the difficulty of obtaining accurate results for $N(E)$ in a band-structure calculation. Such results are particularly sensitive to the way in which flat portions of the energy bands are handled since the density of states is a Fermi-surface average of $1/v$, where v is the magnitude of the Fermi velocity. To achieve significant changes under pressure, band-structure calculations therefore usually employ volume reductions which are huge on the experimental scale. Some typical recent examples are volume reduction steps of 10% for[2] Al and 16% for[3] fcc La. Consequently, direct comparison of the pressure dependence of calculated band-structure properties and experiments has been rare.

In the present paper a new method to make contact between band-structure calculations and experiments is described. We study another Fermi-surface average of the velocity, viz. $\int v\,dS$, both theoretically from a detailed band-structure calculation as well as experimentally from the relation between the pressure dependence of the plasma frequency $\omega(p)$, and the temperature derivative of the electrical resistivity $d\rho(p)/dT$. This relation was studied previously for a number of elemental superconductors[4] but due to the scarceness of appropriate band-structure results qualitative comparison of the result for $\omega(p)$ could be made only for Al and La.

Niobium is chosen for the present investigation for a number of reasons. It is cubic, which facilitates the calculations, $T_c(p)$ has been well determined, and spin fluctuations, which complicate the comparison between calculations and experiments, are apparently no severe problem as, e.g., in V. The results show that there is good agreement between the calculated pressure-induced increase of $\omega(p)$ and that obtained experimentally. Such an agreement serves as a check of our experimental and theoretical methods and permits us to draw further conclusions about the pressure dependence of electron band-structure properties and the electron-phonon interaction $\lambda(p)$.

In Sec. II some useful quantities are defined and it is shown how the pressure dependence of $\omega(p)$ can be obtained from experiments. The pressure experiments are described in Sec. III and results for ρ of Nb are presented as a function of temperature and pressure in the range 0—40 °C and 0—1 GPa. In Sec. IV we obtain an experimental determination of the pressure dependence of $\omega(p)$ for Nb from these experiments and published results for $T_c(p)$ and the compressibility and also discuss the accuracy of this result. The band-structure calculation and results are described in Sec. V. The pressure dependence of a number of Fermi-surface properties are obtained, includ-

ing $\omega(p)$, the density of the electron states, and the optical electron mass, and they are compared to results from the literature where available. By combining our experimental result for $\rho(p,T)$ and calculated result for $\omega(p)$ we obtain an estimate of $\lambda(p)$ for Nb in Sec. VI. The main results are summarized in Sec. VII.

II. THEORY

Our starting point is the definition of the plasma frequency[5]

$$\omega^2=(2e^2/3V\epsilon_0)\sum_{\vec{k}} v^2\delta(E_{\vec{k}}-E_F)$$
$$=(2e^2N/3\epsilon_0V)N(E_F)\langle v^2\rangle\ , \tag{1}$$

where ϵ_0 is the vacuum dielectric constant, v is the Fermi velocity $|\vec{v}(\vec{k})|$, and N is the number of atoms in the crystal volume V. The last member of Eq. (1) defines an expectation value of the Fermi velocity squared $\langle v^2\rangle$, and $N(E_F)$ is the electron density of states at the Fermi level per atom and spin. The sum in Eq. (1) can be transformed to an integral over the Fermi surface

$$\sum_{\vec{k}} v^2\delta(E_{\vec{k}}-E_F)=(V/8\pi^3)\int v\,dS\ . \tag{2}$$

We then obtain a form for the plasma frequency which is suitable for programming,

$$\omega^2=(e^2/12\pi^2\epsilon_0)\int v\,dS\ . \tag{3}$$

The optical effective mass scaled with the free-electron mass is also of interest in transport theory. It is defined as[2]

$$m_{\rm op}/m_0=v_0S_0\Big/\int v\,dS\ , \tag{4}$$

where m_0, v_0, and S_0 refer to the free-electron values. $N(E_F)$ is calculated as the surface integral

$$N(E_F)=(V/8\pi^3N)\int v^{-1}dS\ . \tag{5}$$

$\langle v^2\rangle$ can now be obtained from Eqs. (1), (2), and (5)

$$\langle v^2\rangle=\int v\,dS\Big/\int v^{-1}dS\ . \tag{6}$$

A parameter q is introduced to describe the pressure dependence of $\omega^2(p)$ by the relation

$$\omega^2(p)=\omega^2(0)/(1+q\,\Delta V/V_0)\ , \tag{7}$$

where $\Delta V=V-V_0$ is the volume reduction with pressure. In the limit $p=0$ this definition is equivalent to $q=-d\ln\omega^2(p)/d\ln V$. At arbitrary pressure Eq. (7) is preferred, however, since it reduces to the free-electron-like case in a simple way. For free electrons $\omega^2(p)$ is proportional to the electron number density which scales with volume as $1/V$ and then $q=1$ for all pressures.

q can be obtained from the experiments in the following way. The relation between the resisitivity ρ at a temperature approximately greater than Θ and the electron-phonon interaction is[5]

$$\rho=\frac{3Vk_B}{\hbar e^2N}\frac{1}{N(E_F)\langle v^2\rangle}T\lambda_{\rm tr}\ . \tag{8}$$

$\lambda_{\rm tr}$ differs from the electron-phonon interaction in superconductivity by a factor of the order of unity related to the average of the scattering angle in the transport process. We neglect the pressure dependence of this factor and take $d\lambda/dp=d\lambda_{\rm tr}/dp$. This gives[4] the following expression for $\lambda(p)$:

$$\lambda(p)=\lambda(0)\left[\frac{1+\Delta V/3V}{1+q\,\Delta V/V}\right](1+Bp)\ , \tag{9}$$

where B is the pressure coefficient of the temperature derivative of the resistance as in Eq. (12) below.

T_c is calculated from McMillan's formula[6]

$$T_c=\frac{\Theta}{1.45}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right]\ . \tag{10}$$

Here μ^* is the Coulomb pseudopotential and Θ the Debye temperature. We assume that the pressure dependence of Θ is described by a Grüneisen parameter γ_G

$$\Theta(p)=\Theta(0)(1-\gamma_G\Delta V/V)\ , \tag{11}$$

and take γ_G and μ^* to be constants independent of pressure.

From our experimental result for B and published results for $\Delta V/V$ one can calculate $\lambda(p)$ from Eq. (9) for a given value of q. Our experimental result for q is that value for which the experimental $T_c(p)$ agrees with $T_c(p)$ calculated from Eq. (10) with λ and Θ substituted from Eqs. (9) and (11).

III. EXPERIMENTAL METHODS AND RESULTS

A. Resistance measurements

The sample used for the resistance measurements was cut from a Nb rod (Marz grade, Materials Research Corporation), cold-worked into a wire of square cross-section area 1×1 mm^2, and cleaned by etching in a mixture of HNO_3 and HF. In this condition the residual resistance ratio, $R(290\ \text{K})/R(9.2\ \text{K})$, was about 40, and T_c as measured resistively was 9.16 K. In previous resistance measurements[7,8] on high-purity Nb a considerable improvement of sample quality was achieved by degassing the sample in a high vacuum close to the melting temperature. In the present paper we used the sample in the condition described above since we want to combine resistance measurements with published results for the pressure dependence of $T_c(p)$. Such measurements have been reported[9] for a sample of the same source and quality as that presently studied and with similar zero pressure T_c.

A wire sample of length $\sim$45 mm was mounted into the pressure cell and short lengths of Manganin wire were spot-welded to it to provide current and potential leads that could easily be soldered to the copper wires leading out of the pressure cell. The high-pressure measurements were carried out using the same equipment and the same procedures as in previous investigations.[4,10] The pressure medium used was ethanol of nominal 99.5% purity, the temperature was measured with a Chromel-Alumel thermocouple, and pressure was measured with a Manganin resistance gauge.

The resistance was measured as a function of temperature and pressure in the range 0—40 °C and 0—1 GPa. It

TABLE I. Resistance as a function of temperature and pressure for a Nb sample.

T (°C)	P (GPa)	R (mΩ)	T (°C)	P (GPa)	R (mΩ)
+ 21.63	0.0001	10.592	+ 1.44	0.1395	9.882
22.34	0.065	10.598	11.21	0.149	10.217
22.73	0.135	10.603	34.54	0.155	11.000
22.73	0.235	10.589	36.75	0.156	11.070
22.00	0.237	10.560	37.92	0.249	11.092
22.57	0.368	10.562	39.05	0.3985	11.111
22.02	0.367	10.540	38.23	0.396	11.081
22.02	0.511	10.516	38.15	0.5175	11.057
22.73	0.617	10.528	39.07	0.622	11.075
22.15	0.615	10.505	38.18	0.620	11.043
22.02	0.772	10.473	37.98	0.773	11.010
22.57	0.874	10.476	38.08	0.890	10.995
22.02	0.873	10.453	37.95	1.013	10.966
22.02	1.010	10.433	38.92	1.084	10.988
21.81	1.006	10.423	38.21	1.084	10.962
21.84	0.998	10.424	37.92	1.083	10.952
21.63	0.965	10.429	37.67	1.081	10.942
8.69	0.939	10.005	21.34	0.959	10.422
3.78	0.935	9.844	20.02	0.873	10.390
−2.82	0.935	9.613	21.08	0.871	10.426
4.89	0.948	9.874	20.21	0.753	10.420
3.18	0.944	9.821	21.08	0.756	10.446
2.83	0.943	9.809	20.23	0.585	10.449
1.96	0.864	9.789	21.10	0.585	10.474
1.28	0.7485	9.780	20.02	0.484	10.454
1.74	0.748	9.796	21.10	0.486	10.490
0	0.582	9.760	19.92	0.385	10.470
1.74	0.584	9.821	21.05	0.386	10.503
0.27	0.505	9.780	20.29	0.263	10.500
1.47	0.505	9.830	21.00	0.2625	10.520
1.83	0.393	9.858	20.02	0.129	10.516
0	0.256	9.817	21.16	0.129	10.551
0.90	0.258	9.849	20.02	0.023	10.535
0.22	0.151	9.839	21.16	0.023	10.569
1.17	0.151	9.872			
0.65	0.139	9.853			

would have been preferable to perform these measurements at a few fixed temperatures. However, due to insufficient temperature control, a change of pressure was usually accompanied by a small but significant change of temperature. Therefore, the resistance is given as a function of pressure and temperature in chronological order in Table I. As a check on the equipment and sample the measurements around room temperature were repeated at the end of the experiment. The raw data were checked for consistency as described before[4] which led to the deletion of only a few data points.

B. Analysis of resistance data

The resistance at p and T is obtained as a series expansion from a fixed point taken to be the resistance at 0 °C and the ambient pressure $p=0$. With T in °C

$$R(p,T)=R(0,0)(1+AT)(1+Bp)\ . \tag{12}$$

The best fit of the data of Table I to this expression is shown in Table II. The relative rms deviation of this fit was 3×10^{-4}.

A more general expression than Eq. (12) is

$$R(p,T)=R_0+aT+bp+cpT\ . \tag{13}$$

When fitting the data of Table I to this expression we obtained $R_0=9.855(5)$ mΩ, $a=3.389\times10^{-2}$ mΩ K^{-1}, $b=-1.542\times10^{-1}$ mΩ GPa^{-1}, and $c=-5.07\times10^{-4}$ mΩ K^{-1} GPa^{-1}. The difference between this best fit to Eq. (13) and that to Eq. (12) is a term $2.2\times10^{-5}pT$ mΩ K^{-1} GPa^{-1} which for any p,T in the range studied gives an insignificant contribution to the measured resistance. In the analysis in Sec. IV Eq. (12) is preferred to Eq. (13) since it contains a smaller number of parameters, which are consequently better defined. However, the

TABLE II. Results for the fit of experimental data to Eq. (12).

	$R(0,0)$ (mΩ)	A (10^{-3} K^{-1})	B (10^{-2} GPa^{-1})
Nb	9.855(4)	3.44(6)	−1.56(2)

agreement between Eqs. (12) and (13) supports the important point that we do not impose unphysical restrictions on the data by fitting to Eq. (12). This possibility was discussed previously[4] but we could not then reach a definite conclusion.

We looked for but did not succeed in identifying a higher-order term, Cp^2, in the pressure-dependent factor of Eq. (12). For a range of values of C below 8×10^{-4} the different fits to the experimental data could not be distinguished. Therefore, we conclude that C for Nb is smaller than 8×10^{-4} GPa^{-2} and that measurements at higher pressures are required to determine this coefficient.

The pressure dependence of the resistance of niobium has previously been studied by Bridgman in several experiments, in most cases on rather impure samples. His results for the purest sample,[11] with a temperature coefficient of resistance of 3.05×10^{-3} K^{-1}, can be written as $R(p)=R_0(1-1.43\times10^{-2}p+3.6\times10^{-4}p^2)$, with p in gigapascals. The difference in pressure coefficient relative to our sample is of the sign and magnitude expected from the difference in purity.

For high-purity Nb the temperature coefficient of resistance is higher than the presently observed value. From the results given by Webb[7] for a sample with residual resistance ratio of 16000 we calculate $R^{-1}dR/dT=3.9\times10^{-3}$ K^{-1} at 0°C. For a sample with resistance ratio 210 the temperature coefficient is[8] 3.6×10^{-3} K^{-1}. Our results of 3.44×10^{-3} compare favorably with a handbook value[12] for good standard quality Nb of 3.39×10^{-3} K^{-1}.

IV. EXPERIMENTAL DETERMINATION OF THE PRESSURE DEPENDENCE OF THE PLASMA FREQUENCY

A. Result for q

The following four zero-pressure parameters for Nb are assumed:

(i) $\gamma_G(p)=\gamma_G(0)=1.74$,

(ii) $\mu^*(p)=\mu^*(0)=0.13$,

(iii) $\Theta(0)=280$ K ,

(iv) $\lambda(0)=0.815$.

γ_G is calculated[13] from the lattice specific heat. The value for μ^* is a conventional choice for transition metals.[6] Θ is obtained from the low-temperature specific heat,[14] and the value of λ is chosen so that the observed zero-pressure value for T_c of our sample is reproduced in Eq. (10). This value of λ is close to the traditional result[6] for Nb. Other choices for some of these parameters will be discussed in Secs. IV B–IV D.

The observed pressure dependence of sample volume,[15] $T_c(p)$,[9] and $d\rho(p)/dT$ from the present results are now used to obtain q. We have

$$\Delta V/V=-6.778\times10^{-3}p+2.6\times10^{-4}p^2 , \quad (14)$$

where p is in units of GPa,

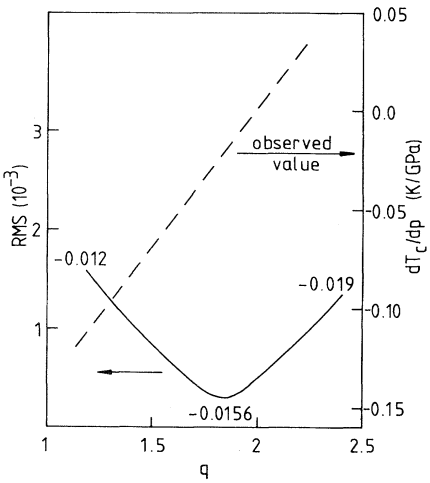

FIG. 1. Illustration of the sensitivity of the experimental result for q to observed values of dT_c/dp and B. The dashed line shows the relation between dT_c/dp and q for our best value of $B=-0.0156$ GPa^{-1}. The observed dT_c/dp from Ref. 9 is marked by an arrow in the figure and corresponds to $q=1.84$. On the full curve $dT_c/dp=-0.021$ K/GPa and B is varied in the range -0.012 to -0.019 GPa^{-1}. For each value of B the experimental data is fitted to Eq. (12) by least squares and the minimum rms deviation of that fit is plotted vs the value of q calculated with the chosen value of B.

$$dT_c/dp=-0.021\pm0.001 \quad (15)$$

in units of K/GPa, and

$$B=-0.0156 \quad (16)$$

in units of GPa^{-1}. Equations (9), (11), and (14)–(16) are inserted into Eq. (10) and $T_c(p)$ is calculated for a series of q values. The observed and calculated depression of T_c at 1 GPa agree for $q=1.84$.

Figure 1 illustrates the sensitivity of this calculation to the experimental results of Eqs. (15) and (16). The dashed line gives the relation between the calculated dT_c/dp and q for $B=-0.0156$ GPa^{-1}. It can be seen that the experimental uncertainty corresponds to a negligible error in q. On the full curve a point (Δ,q) was obtained by choosing a value B and fitting the experimental data to Eq. (12), keeping B fixed and allowing A and R_0 to vary. Δ is the minimum rms value of such a fit and q is the value calculated from the formalism above with $dT_c/dp=-0.021$ K/GPa and the chosen value of B. The full curve is obtained by repeating this calculation for a series of values of B in the range from -0.012 to -0.019 GPa^{-1}. Allowing for an increase by a factor of 2 over the best rms value would correspond to a variation of q of about 0.2. Our experimental result for q can therefore be summarized as $q=1.84\pm0.2$. We now discuss corrections to this result which may arise from errors in the assumptions (i)–(iv) listed above.

B. Phonons

Experimental results for γ_G are generally[13,15,16] within 20% of the value 1.74 chosen above. Such a range for γ_G

comprises results from specific heat, compressibility, and shock-wave experiments which weight the phonon spectrum differently. Therefore, possible different weightings of the phonons in the calculation of $T_c(p)$, e.g., soft phonon mode contributions, would not seem to present any serious problem. A change of γ_G by 20% would change q by less than 8%.

The pressure dependence of γ_G was investigated by Ramakrishnan *et al.*[17] They set $\gamma_G=\gamma_0(V/V_0)^s$ and determined s for several elements but not for Nb. When this effect is taken into account Eq. (11) should be replaced by

$$\Theta=280\left\{1-\frac{1.74}{s+1}\left[\left[\frac{\Delta V}{V}+1\right]^{s+1}-1\right]\right\}. \tag{17}$$

For reasonable values for s of Nb between 0 and 1 the effect on the result for q is negligible. Equation (11) thus seems to account adequately for the pressure dependence of the phonon frequences of Nb and the value chosen for a constant γ_G is not crucial for the result for q.

C. $\mu^*(p)$

The pressure dependence of μ^* is generally believed to be small enough to be neglected. Since, in Nb, dT_c/dp is also small, we must investigate the effect of a reasonable pressure dependence of μ^* on the result for q.

Two methods to estimate $\mu^*(p)$ are examined. The first one is based on a Thomas-Fermi estimate of μ^* by which Smith[18] obtained $d\ln\mu^*/d\ln V=0.27\,d\ln N(E_F)/d\ln V$. The volume dependence of $N(E_F)$ can be obtained from low-temperature thermal expansion measurements. At low temperature one has[5]

$$\gamma_e=\frac{d\ln N(E_F)}{d\ln V}+\frac{\lambda}{1+\lambda}\frac{d\ln\lambda}{d\ln V}, \tag{18}$$

where γ_e is the electronic Grüneisen parameter. Measurements of Nb gave[19] $\gamma_e=1.5$ and from the result for $\lambda(p)$ in Sec. VI one then obtains $d\ln N(E_F)/d\ln V=1.2$.

From Table IV below our calculated result for $d\ln N(E_F)/d\ln V$ in the low-pressure region averages at about 1.1. This agreement is encouraging since the calculated $N(E_F)$ is very sensitive to the chosen value for E_F as discussed in Sec. V B. The estimate of the volume dependence of μ^* which results from this method is therefore

$$\mu^*=0.13(1+0.32\,\Delta V/V_0). \tag{19}$$

Use of this function in the formalism above to calculate q gives $q=1.71$.

The other method to estimate $\mu^*(p)$ is based on a semiempirical fit[20] of values of μ^* to a function of $N(E_F)$. Although this approach accounts only roughly for the magnitude of $\mu^*(0)$ it may give an adequate description of the pressure dependence.[21] We thus take $\mu^*=CN(E_F)[1+N(E_F)]^{-1}$ [with $N(E_F)$ in units (eV atom both spins)$^{-1}$] and adjust C to give $\mu^*(0)=0.13$. With the experimental result $d\ln N(E_F)/d\ln V=1.2$ as above, $\mu^*(p)$ is similar to Eq. (19) and the result for q is 1.69.

Therefore, the broadening of the energy bands under pressure is expected to reduce the electron-electron interactions measured by μ^* and such a reduction leads to a decrease in the resulting value of q. The magnitude of this effect is estimated to be within the 10% uncertainty for q obtained above.

D. Zero-pressure parameters

Results from tunneling spectroscopy[22] and band-structure calculations[23] suggest that $\lambda(0)$ for Nb may be 20—40 % larger than the traditional value calculated from Eq. (10) and the measured T_c and Θ. Since the relative pressure dependence of T_c from Eq. (10) depends on the relative magnitude of the different parameters, we investigate the effect of varying zero-pressure parameters on our result for q.

Within the framework of McMillan's equation an explanation for a high value of $\lambda(0)$, preserving the observed $T_c(0)$, can include one or several of the following effects: (i) an average phonon frequency $\omega_{\log}$ is smaller than $\Theta 1.20/1.45$, (ii) μ^* is larger than 0.13, and (iii) spin fluctuations depress T_c.

Following a calculation of Butler *et al.*[23] we take $\lambda(0)=1.117$, $\mu^*=0.183$, and a low value of $\Theta=203$ K, corresponding to their result for $\omega_{\log}=168$ K multiplied by the ratio of different prefactors in McMillan's formula 1.45/1.20. The result for q is then 1.66. We may instead allow for spin fluctuations by inserting into McMillan's formula a term $+\lambda_{sp}$ in the numerator of the argument of the exponent due to the apparent electron mass enhancement and a term $-\lambda_{sp}$ in the denominator due to the pair-weakening effect of the paramagnons.[24] If we accept the high value of $\lambda_{sp}=0.2$ for Nb obtained by Rietschel and Winter[25] and keep $\Theta=280$ K and $\mu^*=0.13$ we must take $\lambda(0)=1.28$ to get the right $T_c(0)$. In this case one finds $q=1.96$.

These two examples may represent extremal cases for the change of q with the zero-pressure parameters. q of Nb is lower or higher than 1.84 depending on whether one favors an explanation for a high $\lambda(0)$ in terms of a low $\omega_{\log}$ or in terms of spin fluctuations (or a high μ^*). It is not unlikely that both of these effects occur in Nb and hence, to some extent, cancel in the determination of q.

In summary of this discussion of assumptions in the experimental determination of q we find that our result $q=1.84\pm0.2$ is confirmed and strengthened, and that the minus sign in the estimated error of q may have a somewhat higher probability.

V. THE BAND-STRUCTURE CALCULATION

A. Method

The electronic band structure of Nb was calculated self-consistently by means of the linear muffin-tin orbital (LMTO) method.[26] The unit cell volume V was varied so that the fraction V/V_0 ranged from 1.0 to 0.95 in steps of 0.01. V_0 is the experimental zero-pressure volume, corresponding to the lattice constant 3.30 Å.[27] The atomic-sphere approximation[26] (ASA) was used in all the calculations during the iterations to self-consistency. When the LMTO-ASA scheme had converged, we made a final calculation where we included corrections to the ASA. Band calculations including these corrections will be referred to as LMTO calculations. These corrections account for the errors that are introduced when the atomic polyhedron is approximated with a Wigner-Seitz sphere. The full details

of the LMTO and LMTO-ASA methods, including error estimates and accuracy, can be found in Ref. 26.

Niobium has the atomic configuration [Kr]$4d^4 5s^1$. We kept the krypton core frozen in the band-structure calculations. Our present LMTO computer code is semirelativistic, i.e., the mass velocity and the Darwin terms are included in the Hamiltonian, but the spin-orbit coupling is omitted. The most important relativistic effects are thus taken into account without enlarging the Hamiltonian and overlap matrices.

We calculated the bands in 54 points in the irreducible Brillouin zone (BZ), using a grid with $\Delta k = \frac{1}{8}$ (k is in units of 2π divided by the lattice constant). This is equivalent to 1023 points in the whole BZ, when the cubic crystal symmetry is considered. The center of the Brillouin zone, $\vec{k}=(0,0,0)$, must be excluded from the LMTO calculations because the Neumann function is singular there. The energy levels for $\vec{k}=(0,0,0)$ were determined by quadratic extrapolation from $\vec{k}=(\frac{1}{8},0,0)$ and $\vec{k}=(\frac{1}{4},0,0)$.

The iteration process was started from potentials calculated from renormalized free atoms. The new potential for iteration $i+1$ was calculated in a potential mixing scheme from $V_{i+1}(r)=0.20V_i+0.80V_{i-1}$. A converged solution to the Schrödinger equation is obtained in 20–30 iterations. The wave functions were calculated in an energy grid of 30 steps from the bottom of the bands up to the Fermi level.

The choice of an exchange-correlation approximation is one of the important steps in a band-structure calculation. In the present work we used the Hedin-Lundqvist[28] model for both the core and the valence electrons. This approximation is known to give a good description of the ground-state properties of metals.[29]

In order to calculate the density of states and the Fermi energy, it is necessary to know the bands at a large number of $\vec{k}$ points. After a self-consistent solution was achieved, we interpolated the bands using a 27-point Lagrange formula to a grid with $\Delta k = \frac{1}{96}$. At the same time the gradients $\vec{\nabla}_{\vec{k}} E(\vec{k})$ were calculated. From the interpolated bands the Fermi energy and the density of the electron states were calculated with the Gilat-Raubenheimer method.[30]

B. Results for the zero-pressure band structure

Our calculated band structure is in close correspondence with previously published calculations.[29,31–33] This conclusion is, however, only valid when we include corrections to ASA in the calculations. The LMTO results at some selected $\vec{k}$ points are given in Table III. One of the more noticeable differences between the LMTO and LMTO-ASA bands is that Γ'_{25} is an occupied state in the ASA, whereas in the LMTO case it is placed above the Fermi level. The Γ'_{25} shift is as large as 0.48 eV. The LMTO-ASA is thus in disagreement with other calculations,[29,31–33] and we conclude that it is necessary to include corrections to the ASA in order to achieve a reliable result.

In the Nb metal we obtained the configuration [Kr]$4d^{3.67}5s^{0.65}5p^{0.68}$ when the wave functions are analyzed in a spherical harmonics representation. The density of the electron states at the Fermi level, $N(E_F)$, is difficult to calculate with high accuracy since $N(E)$ is very sensitive to small variations in the Fermi energy. The density of states is rapidly falling at the Fermi level: $dN(E_F)/dE = -356$ Ry^{-2}, in good agreement with the value -350 Ry^{-2} reported by Elyashar and Koelling.[32]

Our LMTO result for $N(E_F)$ of Nb is 10.9 states/Ry atom spin. This is well within the range of values obtained in recent band-structure calculations which include the following (in units of states/Ry atom spin): Chakraborty *et al.*,[34] 9.2; Boyer *et al.*,[35] 9.0–10.5; Butler *et al.*,[36] 9.9; Elyashar and Koelling,[32] 11.2; Varma *et al.*,[37] 11.5; Anderson *et al.*,[31] 14.1; Ho *et al.*,[33] 15.0. If the corrections to ASA are not included in our calculation we obtain 14.7 states/Ry atom spin which is on the high side of this range of values. An empirical estimate of $N(E_F)$ can be obtained from the measured electronic contribution γ to the low-temperature specific heat and a value for the mass enhancement factor $1+\lambda$. With experimental results for γ of[13] 7.66 or[14] 7.80 mJ/mol K^2 and values of λ in the range 0.8–1.1 the empirical value for $N(E_F)$ is in the range 10.5–12.5 states/Ry atom spin.

The plasma frequency ω is rather insensitive to small variations of the Fermi level. This is evident from Fig. 2, where we show ω^2, $N(E_F)$, and $\langle v \rangle^2$ on an expanded energy scale around the Fermi energy. $N(E)$ varies by 25% over a 10-mRy energy range, in contrast to ω which varies with only 2%. This conclusion is similar to that reached previously for Mo by Chakraborty *et al.*[34]

The rms value for the Fermi velocity, $\langle v^2 \rangle^{1/2}$, is found to be 0.55×10^8 cm/sec, which is in good agreement with the values 0.61×10^8 cm/sec reported by Chakraborty *et al.*[34] and 0.51×10^8 cm/sec obtained by Varma *et al.*[37]

TABLE III. Energy levels at some selected points for different values of V/V_0 (in eV, $E_F=0$).

V/V_0	Γ_1	Γ'_{25}	H_{12}	N_1	N_2	P_4
1.00	−6.15	0.38	−4.14	−3.96	−1.65	−1.19
0.99	−6.19	0.37	−4.23	−4.03	−1.70	−1.22
0.98	−6.22	0.35	−4.31	−4.10	−1.74	−1.24
0.97	−6.26	0.34	−4.39	−4.15	−1.79	−1.25
0.96	−6.29	0.33	−4.49	−4.22	−1.84	−1.27
0.95	−6.33	0.30	−4.57	−4.29	−1.88	−1.29
1.00[a]	−5.26	0.31	−4.11	−3.71	−1.74	−1.05

[a]Reference 29.

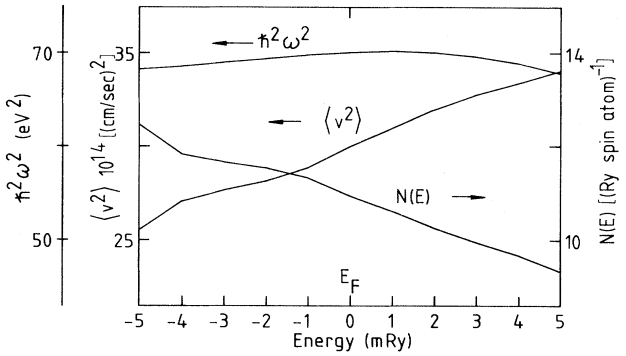

FIG. 2. Results for $N(E_F)$, $\langle v^2 \rangle$, and ω^2 from the band-structure calculation (corresponding to zero pressure) illustrating the point that although $N(E_F)$ and $\langle v^2 \rangle$ are both sensitive to the choice of E_F on a mRy scale, their product ω^2 is not.

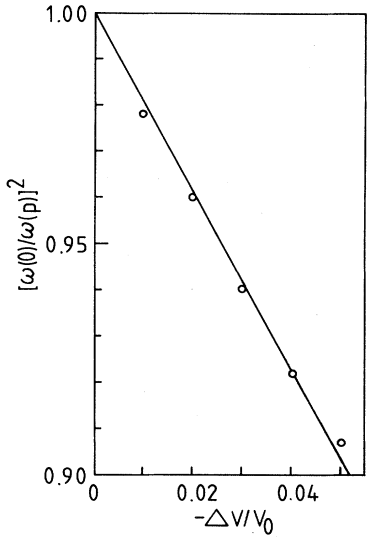

FIG. 3. Determination of q from the band-structure calculation. By Eq. (7) the slope of the straight line approximating the data gives $q = 1.95 \pm 0.1$.

Our result for the plasma frequency of $\hbar\omega = 8.38$ eV is also comparable to a previous calculation by Chakraborty *et al.*[34] of 8.87 eV.

C. The band structure under pressure

The results for the energy shifts under pressure of some selected points in the Brillouin zone are given in Table III and the results for the volume dependence of several Fermi surface properties of Nb are given in Table IV. Closer inspection of these data shows that the variation with volume is comparatively smooth. The numerical scatter in thus not serious even at these small volume reductions.

To our knowledge there is only one published band-structure calculation for Nb performed for different lattice parameters, where Anderson *et al.*[31] made calculations for $a = 0.95a_0$. In the present work a is at most reduced to $0.983a_0$. Nevertheless, the value of $d\ln N(E_F)/d\ln V$ calculated by us from the results of Ref. 31 is 1.3, which is similar to our result.

q is determined from Table IV and Eq. (7) by plotting $\omega^2(0)/\omega^2(p)$ vs $\Delta V/V_0$ as in Fig. 3. It is seen that a straight line approximates the data satisfactorily, which demonstrates that it is useful to define q as in Eq. (7). The result is $q = 1.95 \pm 0.1$, where the error is estimated from the scatter of the slopes of the straight lines fitted to different subsets of the data. A systematic error from the various approximations of the band-structure calculation is difficult to estimate. It is encouraging, however, that the result from our preliminary LMTO-ASA calculation[38] of $q = 1.85 \pm 0.1$ is close to the present LMTO result. This would suggest that q is not particularly sensitive to various details in the band structure in contrast, e.g., to spectroscopic properties.

VI. $\lambda(p)$

By combining our experimental result for B and band-structure calculation of q, one obtains $\lambda(p)$ from Eq. (9). With the use of the experimental compressibility from Eq. (14), the result is

$$\lambda(p) = \lambda(0)(1 - 0.0047p) , \tag{20}$$

with p in gigapascals.

It can be seen that $d\ln\lambda/dp$ is only about one-third of B for Nb. For nontransition metals $|d\ln\lambda/dp|$ is typically 80–90% of B.[4] This is characteristic for the difference between s-p metals and transition metals under pressure. In the early transition metals the smaller pressure coefficient of resistance causes the pressure dependence of $\omega(p)$ to become more important.

The small change of $\lambda(p)$ with pressure obtained by Eq. (20) would be very difficult, or even unfeasible, to determine from inversion of tunneling data. Revenko and co-

TABLE IV. Volume dependence of $N(E_F)$, ω, m_{op}/m, and $\langle v^2 \rangle^{1/2}$ for Nb.

V/V_0	Lattice constant (Å)	$N(E_F)$ [(Ry spin atom)$^{-1}$]	$\hbar\omega$ (eV)	m_{op}/m	$\langle v^2 \rangle^{1/2}$ (10^8 cm/sec)
1.00	3.300	10.94	8.38	1.095	0.547
0.99	3.289	10.86	8.47	1.082	0.553
0.98	3.278	10.67	8.55	1.073	0.560
0.97	3.267	10.50	8.64	1.062	0.568
0.96	3.255	10.26	8.72	1.052	0.577
0.95	3.244	10.04	8.80	1.045	0.585

workers,[39] e.g., failed to detect any change of λ in a hydrostatic experiment to 0.6 GPa.

Furthermore, the result of Eq. (20) for $\lambda(p)$ is independent of a number of requirements, such as the measured $T_c(p)$, an assumption about μ^*, the choice of a suitable γ_G, and McMillan's equation, one or more of which usually enters in other results for $\lambda(p)$. Our result, on the other hand, is based on Eq. (9) and the approximations of the band-structure calculation.

If we want to check the result of Eq. (20) by using McMillan's equation and comparing to the observed $T_c(p)$ we get immediately from Fig. 1 that $q=1.95$ corresponds to $dT_c/dp \approx -0.01$ K/GPa. The difference of 0.01 K/GPa between this value and the observed result may, however, depend not only on small inadequacies of Eq. (20) but also on the various problems in applying McMillan's formula, which were discussed in Sec. IV.

VII. CONCLUSION

The pressure dependence of $\omega(p)$, which is described by the parameter q of Eq. (7), has been determined for Nb by two different approaches. One is an experimental method using the measured pressure dependence of $d\rho(p)/dT$ and published results for $T_c(p)$ and the compressibility; the other is a theoretical method employing a self-consistent LMTO band-structure calculation. The results are within $q=1.9\pm0.06$ for both methods. This agreement is the main result of the present paper since it suggests a novel method to make contact between band-structure calculations and experiments. As a particular example we obtained an estimate of the small pressure dependence of $\lambda(p)$ for Nb using the calculated q, the measured $d\rho(p)/dT$, and published results for the compressibility.

This method would not be expected to be limited to superconductors. The point of the present paper is rather that the consistency of the experimental and theoretical methods can most conveniently be checked by using McMillan's formula and the measured $T_c(p)$.

The necessity of using a hydrostatic pressure medium in order to get reliable results for $d\rho(p)/dT$ was demonstrated by our earlier measurements[4] on double hcp La. Published band-structure calculations have usually employed large volume reductions which are well beyond the experimental possibilities for a hydrostatic experiment with most metallic samples. Therefore, it is worth emphasizing that our calculations were performed for small volume reductions and in several steps, each of 1% volume change, in order to average over the numerical scatter in this low-pressure region. This provides a much more meaningful comparison with the hydrostatic experiments, which in our case extend to 0.7% volume reduction. Our results for the pressure dependence of the density of states, the average Fermi velocity, and the optical mass are therefore expected to be useful for direct comparison with experiments on other transport properties of Nb under pressure.

ACKNOWLEDGMENTS

We are grateful to G. Grimvall for valuable comments on the manuscript. Part of this work has been supported by Naturvetenskapliga Forskningsrådet.

[1]See, e.g., I. V. Svechkarev and A. S. Panfilov, Phys. Status Solidi B 63, 11 (1974); J. P. Franck, W. J. Keeler, and T. M. Wu, Solid State Commun. 7, 483 (1969).
[2]J. Cheung and N. W. Ashcroft, Phys. Rev. B 20, 2991 (1979).
[3]W. E. Pickett, A. J. Freeman, and D. D. Koelling, Phys. Rev. B 22, 2695 (1980).
[4]Ö. Rapp and B. Sundqvist, Phys. Rev. B 24, 144 (1981).
[5]G. Grimvall, *The Electron-Phonon Interaction in Metals* (North-Holland, Amsterdam, 1981).
[6]W. L. McMillan, Phys. Rev. 167, 331 (1968).
[7]G. W. Webb, Phys. Rev. 181, 1127 (1969).
[8]J. M. Abŕaham and B. Deviot, J. Less-Common Met. 29, 311 (1972).
[9]T. F. Smith and R. N. Shelton, J. Phys. F 5, 911 (1975).
[10]B. Sundqvist and Ö. Rapp, J. Phys. F 9, L161 (1979).
[11]P. W. Bridgman, Proc. Am. Acad. Arts Sci. 73, 149 (1951).
[12]G. T. Meaden, *Electrical Resistance of Metals* (Heywood, London, 1965), p. 16.
[13]K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964).
[14]Y. Kimura, T. Ohtsuka, T. Matsui, and T. Mizusaki, Phys. Lett. 29A, 284 (1969).
[15]S. N. Vaidya and G. C. Kennedy, J. Phys. Chem. Solids 33, 1377 (1972).
[16]The value $\gamma_G=7.09$ calculated from the compressibility data of Ref. 15 is apparently anomalously high.
[17]J. Ramakrishnan, R. Boehler, G. H. Higgins, and G. C. Kennedy, J. Geophys. Res. 83, 3535 (1978).
[18]T. F. Smith, J. Phys. F 2, 946 (1972).
[19]G. K. White, Cryogenics 2, 292 (1962).
[20]K. H. Benneman and J. W. Garland, in *Superconductivity in d- and f-band Metals (Rochester),* Proceedings of the Conference on Superconductivity in *d*- and *f*-Band Metals (AIP, New York, 1972), Vol. I, p. 103ff.
[21]D. A. Papaconstantopoulos and B. M. Klein, Physica 107B, 725 (1981).
[22]G. B. Arnold, J. Zasadzinski, J. W. Osmun, and E. L. Wolf, J. Low Temp. Phys. 40, 225 (1980).
[23]W. H. Butler, F. J. Pinski, and P. B. Allen, Phys. Rev. B 19, 3708 (1979).
[24]M. A. Jensen and K. Andres, Phys. Rev. 165, 545 (1968).
[25]H. Rietschel and H. Winter, Phys. Rev. Lett. 43, 1256 (1979).
[26]O. K. Andersen, Phys. Rev. B 12, 3060 (1975).
[27]C. Kittel, *Introduction to Solid State Physics,* 5th ed. (Wiley, New York, 1976), p. 31.
[28]L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).
[29]V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).
[30]G. Gilat and L. J. Raubenheimer, Phys. Rev. 144, 390 (1966).
[31]J. R. Anderson, D. A. Papaconstantopoulos, J. W. McCaffrey, and J. E. Schreiber, Phys. Rev. B 7, 5115 (1973).
[32]N. Elyashar and D. D. Koelling, Phys. Rev. B 13, 5362 (1976).
[33]K. M. Ho, S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 15, 1755 (1977).
[34]B. Chakraborty, W. E. Pickett, and P. B. Allen, Phys. Rev. B 14, 3227 (1976).
[35]L. L. Boyer, D. A. Papaconstantopoulos, and B. M. Klein, Phys. Rev. B 15, 3685 (1977).
[36]W. H. Butler, F. J. Pinski, and P. B. Allen, Phys. Rev. B 19,

3708 (1979).
[37]C. M. Varma, E. I. Blount, P. Vashishta, and W. Weber, Phys. Rev. B 19, 6130 (1979). There seems to be an error in Table II in this paper: The units for $\langle v^2 \rangle$ must be 10^{16} (cm/sec)^2.
[38]J. Neve, B. Sundquist, and Ö. Rapp, Third European Physical Society Meeting on Condensed Matter Physics, Lausanne, 1983 (unpublished).
[39]Yu. S. Revenko, A. I. D'yachenko, V. M. Svistunov, and B. Shonaikh, Fiz. Nizk. Temp. 6, 1304 (1980) [Sov. J. Low Temp. Phys. 6, 635 (1980)].