Pressure dependence of the electron-phonon interaction and the normal-state resistivity

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Accurate measurements of the electrical resistance as a function of temperature and pressure are reported for Sn, Zr, dhcp La, and V. These measurements cover a temperature region around room temperature and pressures up to 1.3 GPa. From these data, including also our previous measurements for Al and published results for Pb, the pressure dependence of $d\rho/dT$ (the resistivity-temperature derivative) is obtained. This quantity is found to be a significant factor in the pressure dependence of the electron-phonon interaction parameter λ. For the nontransition metals the relative pressure dependence of $d\rho/dT$ is much larger than the compressibility. Therefore the pressure dependence of the superconducting T_c is quantitatively well accounted for by the resistance data for these metals. For the transition metals the pressure dependence of $d\rho/dT$ is relatively smaller and $T_c(p)$ calculated from the resistance data is, at the best, only qualitatively correct. These differences are discussed. Estimates for the pressure dependence of the plasma frequency are obtained.

I. INTRODUCTION

The well-known relation between the electron-phonon interaction λ and the normal-state electrical resistivity ρ provides a very useful method to study superconducting elements and alloys. Several examples are given in a new monograph.[1] For example, it has been shown[2] that the pressure dependence of λ can be accurately measured in Al by the pressure and temperature dependence of ρ.

In the present paper this method is extended and applied to several superconducting elements. We obtain results for $\lambda(p)$ for these metals and also use a combination of measurements under pressure of the superconducting transition temperature, T_c, and $d\rho/dT$ to estimate the pressure dependence of the plasma frequency connecting the electron-phonon interaction in superconductivity and transport theory.

The measurements of the resistance of Sn, Zr, La, and V as a function of temperature and pressure are described in Sec. II. These measurements cover a temperature region around room temperature and pressures up to 1.3 GPa. It is customary in the literature to present such results as the pressure dependence of the resistance at various fixed temperatures. In an experimental situation, however, there is usually a small change in temperature when the pressure is changed even when efforts are made to obtain good thermal contact with a surrounding bath. With the high accuracy aimed at presently we take this into account and present our results (with the exception of La, to be described) in the form of tables with the measured resistance as a function of temperature and pressure. In the analysis in Sec. III it is described how the pressure dependence of $d\rho/dT$ and λ are obtained from these data. In Sec. IV the results for $\lambda(p)$ are given. Results from the literature for Pb and our previous results for Al are included in this analysis. Using McMillan's formula[3] these results are compared with results from the literature for the observed variation of T_c with pressure. This is the most reliable source of information on superconducting parameters under pressure. In Sec. V we discuss some of the approximations used in the previous calculations and obtain estimates for the pressure dependence of the plasma frequency. A short summary of the main results are given in Sec. VI.

II. EXPERIMENTAL DETAILS AND RESULTS

A. Sample characterization

The source and nominal purity of the elements used are specified in Table I. The Sn and V samples were obtained in the form of wires with diameters of 1.2 and 0.5 mm, respectively. As for Zr a rod was cold worked into a band of cross section of 1.7×0.06 mm^2. Annealing was attempted in a vacuum of 10^{-7} torr and at various temperatures in the range

TABLE I. Elements used.

Element	Nominal purity (wt.%)	Source
Sn	99.999	Materials Research Corp. N.Y.
Zr	99.99 (excl. Hf)	Materials Research Corp. N.Y.
La	99.9	Koch Light Ltd. England
V	99.95	Materials Research Corp. N.Y.

1250–1400 °C but it was found that the residual resistance ratio, RRR, did not improve significantly under these conditions. Therefore the cold-worked sample, with an RRR value of 14, was used in the pressure measurements. The crystal structure of La at room temperature is double hcp (dhcp) and converts at zero pressure to a fcc phase above about 200 °C. We measured the resistance in the ^{4}He temperature region of our La sample as received and found $T_c = 5.05$ K. This is in the range of values reported for the T_c of dhcp La which include[4] 4.9 and[5] 5.2 K. After annealing at 370 °C for 3 h and water-quenching T_c was 6.0 K characteristic for the fcc phase. In a resistive measurement even small amounts of a high-T_c phase could be expected to significantly influence T_c. Therefore we take these results as a good indication that our La sample as received was predominantly in the dhcp phase. The RRR of this sample was found to be 35.

B. Pressure measurements

The high-pressure experiments were carried out in the same 45-mm piston and cylinder equipment as used previously.[2] In most of the present experiments the pressure medium used was ethanol of nominal purity 99.5%. In the measurements on La, however, we chose to use *n*-pentane to avoid the possible inclusion of water together with the highly reactive sample in the cell. Pressure was measured using a self-supporting annealed manganin wire gauge, calibrated at several pressures against the melting line[6] of Hg. The temperature was measured with a Chromel-Alumel thermocouple in thermal contact with the sample. The thermocouples were batch calibrated against a standard platinum resistance thermometer.

The resistance of the sample was measured in a standard four-probe arrangement using a simple electronic ac bridge circuit. The sample current was only about 10 mA, and thus the maximum power dissipated in any sample was less than 10 μW. Due to the low current the resolution varied between 0.01 and 0.03% for different samples. The contacts to the samples were made in different ways on different materials. In the case of V, thin Constantan wires were spot welded to the sample. The Sn sample was provided with Cu current leads, soldered directly to the sample, while the potential leads were tinned Cu wires, spot welded in place. Contacts to the thin Zr sample were made by gold-bonding.

The measurements on La posed some problems. Attempts to solder this material were not successful. After several attempts, however, it was possible to form good contacts on a sample using conducting epoxy (Eccobond 45C) and thin Cu wires, working under oil. These contacts were satisfactory at atmospheric pressure but failed at 0.45 GPa, probably because of the large difference in compressibility between La and epoxy. A new attempt was then made using mechanical contacts. Four spring-loaded knife-edge contacts of hardened beryllium-copper were mounted on a common nylon base and screwed down through the oxide layer into the sample, providing good electrical contact. Resistance readings under pressure, however, proved highly irregular with large discontinuities in $R(p,T)$. This was traced to the difference in compressibility between the sample and the nylon holder. The latter was compressed by several percent under pressure, so that the contacts were slightly displaced. It was found, however, that the temperature coefficient of R at constant p could be measured with good precision, since the relative volume changes with T between 0 and 20 °C were negligible at all pressures. Later the nylon base was divided into two parts, which further improved the reproducibility of these measurements.

Due to these problems we cannot present a single set of data from one sample of La covering both $R(p)$ and $R(T)$, as for the other metals investigated. However, in Fig. 1 we show the temperature coeffi-

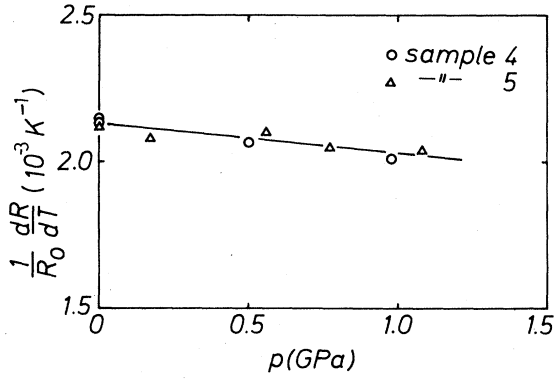

FIG. 1. The temperature coefficient of resistance as a function of pressure for dhcp La.

cient of R $[1/R(T=0\,°C)]$ dR/dT measured between 0 and 20 °C and at pressures up to 1.1 GPa for our samples 4 and 5. As can be seen from the figure, the temperature coefficient of R varies strongly with p (or, equivalently, the pressure coefficient of R varies with T). The pressure coefficient of R was only measured to 0.4 GPa. Within this range R was found to vary linearly with p to within the experimental error. From these data we have synthesized a table of the relative $R(p,T)$ of dhcp La between 0 and 30 °C and (extrapolated) up to 1 GPa.

C. Experimental results

The consistency of the results was checked in different ways. The measured resistance values were reduced by an average temperature coefficient of resistance to one temperature and plotted versus pressure to identify possible erroneous data points. The deviations from the fits, to be described in Sec. III, were checked to be uniformly distributed in the data. These procedures led to the removal of only a few data points.

The coordinates of the R,p,T data are given in Table II in the sequence in which they were obtained (with the exception of La as discussed above). We believe that these results (with the possible exception of La) are of high quality and therefore have an interest of their own. In the present context we use these data to obtain the pressure dependence of λ in Sec. IV and that of the plasma frequency in Sec. V.

Our results for La can be compared to those of other investigations. The temperature coefficient of R at $p=0$ as discussed above is 2.13×10^{-3} K^{-1}, in very good agreement with that found earlier[7] for dhcp La. The pressure dependence of R was investigated at 30 and 75 °C by Bridgman,[8] who found that

TABLE II. Resistance as a function of temperature and pressure for samples of the elements investigated.

T (°C)	p (GPa)	R (mΩ)	T (°C)	p GPa	R (mΩ)
			Sn		
21.63	0	4.372	−19.49	1.0145	3.352
21.68	0.2505	4.270	−19.78	1.010	3.349
21.50	0.2465	4.268	−12.38	0.773	3.532
21.63	0.499	4.170	−18.38	0.7525	3.447
21.47	0.487	4.172	−18.64	0.749	3.444
21.63	0.768	4.070	−19.52	0.514	3.501
21.52	0.758	4.072	−19.78	0.497	3.502
21.68	1.012	3.985	−20.09	0.253	3.577
21.68	1.277	3.896	−20.09	0.251	3.578
21.81	1.293	3.894	−19.09	0.241	3.597
1.36	1.288	3.585	−16.70	0.235	3.638
1.12	1.276	3.585	−10.50	0.240	3.736
0.63	1.228	3.591	0	0.2225	3.914
0.05	1.027	3.644	10.76	0.236	4.086
−0.27	1.009	3.644	20.79	0.255	4.248
0.05	1.0185	3.646	21.68	0.251	4.264
1.12	0.979	3.675	21.68	0.2545	4.263
0.57	0.755	3.739	21.47	0.254	4.260
0.68	0.753	3.741	20.71	0.510	4.151
0.68	0.525	3.819	20.45	0.507	4.144
0.74	0.501	3.828	20.81	0.761	4.053
0.60	0.261	3.913	20.55	0.753	4.051
0.41	0.238	3.918	21.60	1.011	3.977
0.65	0.235	3.923	21.29	1.0005	3.977
−0.08	1.233	3.578	21.47	1.252	3.893
−0.05	1.2525	3.572	21.13	1.237	3.894
0.93	1.261	3.585	21.18	1.307	3.871
−19.21	0.9365	3.378	21.37	1.071	3.954
−19.32	1.034	3.349	22.23	1.0685	3.969

TABLE II (*Continued*).

T (°C)	p (GPa)	R (mΩ)	T (°C)	p GPa	R (mΩ)
			Zr		
19.21	0	89.13	44.92	1.260	96.96
19.10	0.261	89.02	44.86	1.242	96.96
19.13	0.495	88.90	45.40	1.000	97.26
19.31	0.728	88.95	45.24	0.980	97.21
19.26	0.751	88.90	45.42	0.762	97.36
19.42	0.995	88.93	45.37	0.743	97.34
19.47	1.252	88.88	45.34	0.488	97.45
19.44	1.230	88.87	44.28	0.430	97.15
21.58	1.314	89.52	44.71	0.223	97.31
30.36	1.2385	92.32	44.89	0.217	97.37
			44.49	0.761	97.08
			La $R(p,T)/R(0,0)$		
T(°C)		0	10	20	30
	0	1.0000	1.0213	1.0426	1.0639
p(GPa)	0.5	0.9959	1.0167	1.0374	1.0582
	1.0	0.9919	1.0121	1.0322	1.0524
			V		
20.26	0	21.30	−1.34	0.463	19.58
20.00	0.255	21.175	−24.89	0.2305	17.95
20.16	0.482	21.11	−24.49	0.474	17.92
20.13	0.705	21.03	−23.88	0.723	17.90
20.24	0.7625	21.02	−22.56	0.961	17.925
20.21	0.987	20.94	−22.10	1.009	17.95
20.21	1.017	20.93	40.78	0.514	22.57
20.24	1.267	20.85	40.45	0.9855	22.37
20.21	1.253	20.85	40.78	1.261	22.30
−1.48	1.086	19.38	40.78	0.987	22.39
−1.75	0.992	19.385	40.68	0.752	22.47
−1.70	0.7645	19.46	40.48	0.728	22.46
−1.37	0.716	19.50	40.78	0.492	22.57
−1.01	0.518	19.59	40.60	0.473	22.565
−1.34	0.476	19.57	39.86	0.2265	22.61
−1.89	0.236	19.61	40.63	0	22.76

the pressure coefficient of R was small and varied strongly with T. His value at 30 °C, -1.12×10^{-2} GPa^{-1}, is in good agreement with our result at this temperature (-1.09×10^{-2} GPa^{-1}). It should be noted that Bridgman measured $R(p)$ for La on several occasions. Judging from his reported values of the temperature coefficient of R, however, his samples in most cases were not pure dhcp La but also contained a proportion of fcc La (or other impurities). Balster and Wittig[9] report a positive pressure coefficient of R at room temperature. Unfortunately their measurements were taken in a solid (nonhydrostatic) medium, and their results thus cannot be directly compared to the present results.

III. ANALYSIS

A. Pressure dependence of $d\rho/dT$

Considering changes in the temperature and pressure to be small disturbances on the resistance one can calculate the resistance at p and T, $R(p,T)$, by a series expansion from some fixed point. We take

this fixed point to be $T=0\,^{\circ}\mathrm{C}$ and the ambient pressure $p=0$ and write with T in degrees Celsius

$$R(p,T)=R(0,0)(1+AT)[1+Bp(+Cp^2)] \quad . \qquad (1)$$

Our data were fitted by nonlinear least-squares analyses to expressions of this form. For Sn and V a quadratic term in p was included which was found to be adequate for Sn and insignificant for V. For Zr B of Eq. (1) was too small and for La the number of data points too limited to enable C to be determined and C was put $=0$. A linear temperature dependence of the resistance is in general a good approximation in the temperature region presently considered. For Sn however it was found that adding a term $\sim T^2$ in Eq. (1) improved the fit. Since this term is small it has been neglected in the analysis in Sec. III B.

For most metals A of Eq. (1) is positive and B negative so that in these cases the quantity $d^2\rho/dTdp$, which is of interest in the analysis of the pressure dependence of λ, is always negative. There does not appear to be an obvious physical reason for the negative sign of $d^2\rho/dTdp$. Therefore we are also led to consider a more general expression than Eq. (1):

$$R(p,T)=K+aT+bp+cpT \quad . \qquad (2)$$

Unfortunately Eq. (2) with four free parameters [or six when C of Eq. (1) is nonzero] is too flexible for the present experimental accuracy. This point is illustrated in Fig. 2 for Zr. The Zr data are fitted to Eq. (2) and the rms deviation of the fit is plotted as a function of c. When the same data are fitted to Eq. (1) the parameter to be compared with c is R_0AB which is shown by the arrow in the figure. The horizontal line marks the magnitude of the experimental error. It is seen that with a reasonable probability a range of c values, corresponding to the full curve below the error line, is consistent with the experimental data and Eq. (2) and that R_0AB is within this range. The conclusion from Fig. 2 is thus that

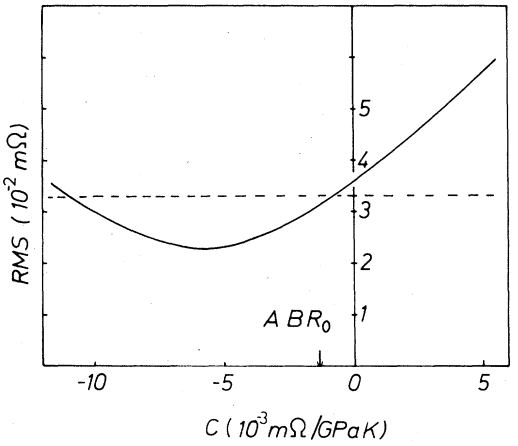

FIG. 2. Analysis of the Zr data. When the Zr data of Table II are fitted to Eq. (2) the full curve describes the rms deviation of the fit as a function of the parameter c of Eq. (2). When the same data are fitted to Eq. (1) the value of the parameter ABR_0 has the value shown by the arrow. The experimental error is shown by the horizontal dashed line.

$d^2\rho/dTdp$ is most likely negative for Zr and that it is preferable to fit the data to Eq. (1) rather than to Eq. (2) due to the limited experimental accuracy. The results have been summarized in Table III.

For Sn, C in Eq. (1) was found to be $+8.06\times10^{-3}$ $(\mathrm{GPa})^{-2}$ and the coefficient of the T^2 term $+2.44\times10^{-6}$ (K^{-2}). The relative rms deviations are about 3×10^{-4} of the measured resistance for all four elements. For convenient reference values for the compressibility[10,11] $\kappa=-(1/V)(dV/dp)$ and the Grüneisen γ_G calculated from specific-heat data[12] are given in Table III. For comparison, previous data[2] for Al and data for Pb obtained from[13,14] average pressure coefficients to 7 kbar at three fixed temperatures in the range 77–300 K have also been included.

TABLE III. Summary of the analysis.

Element	A $(10^3\,\mathrm{K}^{-1})$	B $[10^2(\mathrm{GPa})^{-1}]$	κ $[10^2(\mathrm{GPa})^{-1}]$	γ_G[a]
Al	4.69[b]	−4.25[b]	1.26[c]	2.1
Sn	4.21	−9.56	1.82[c]	2.2
Pb	3.83[d]	−13.1[d]	2.36[c]	2.8
Zr	3.89	−0.36	0.97[e]	0.8
La	2.12	−0.81	4.06[c]	0.7
V	3.63	−1.61	0.70[e]	1.5

[a]Reference 12. [b]Reference 2. [c]Reference 10. [d]Evaluated from Refs. 13 and 14. [e]Reference 11.

B. Pressure dependence of λ

The relation between the high-temperature resistivity and the electron-phonon interaction can be written[1]

$$\rho = \frac{3k_B}{\hbar e^2}\frac{1}{N(\epsilon_F)\langle v^2\rangle} T\lambda_{\rm tr} \ , \tag{3}$$

where $N(\epsilon_F)$ is the number of electron states per unit crystal volume and unit energy at the Fermi energy and $\langle v^2\rangle$ is the average over the Fermi surface of the electron velocity squared. These quantities define the plasma frequency

$$\omega_p^2 = \frac{8\pi e^2}{3} N(\epsilon_F)\langle v^2\rangle \tag{4}$$

used frequently in work on transport and superconductivity.[15] $\lambda_{\rm tr}$ in Eq. (3) is closely related to the electron-phonon interaction λ in superconductivity and differs from this quantity by a factor which for an isotropic system reduces to $\langle 1-\cos\theta\rangle$, θ being the scattering angle in the transport process. We assume that the pressure dependence of this factor is negligible, thus taking $d\lambda/dp = d\lambda_{\rm tr}/dp$. As for the pressure dependence of the plasma frequency we note that the pressure dependence of $N(\epsilon_F)$ can be obtained from various experiments and published band-structure calculations but $\langle v^2\rangle$ and its pressure dependence are seldom calculated. In a free-electron model $d\ln\omega_p^2/dp = +\kappa$. More generally therefore we write (for the low-pressure limit)

$$\frac{d\ln N(\epsilon_F)\langle v^2\rangle}{dp} = q\kappa \tag{5}$$

defining a number q, which thus for a free-electron-like system is $+1$.

The relation between resistance and resistivity is

$$\rho(p) = \text{const} R(p)\left(1+\frac{\Delta V}{3V}\right) \ . \tag{6}$$

The influence of thermal expansion on the conversion between resistance and resistivity is neglected since the range of temperature variation is small.

From these considerations the pressure dependence of λ can be evaluated. From Eq. (3) $\lambda = \text{const} N(\epsilon_F)\langle v^2\rangle d\rho/dT$ and using Eqs. (1), (5), and (6) we write

$$\lambda(p) = \lambda(0)\left(\frac{1+\frac{1}{3}\Delta V/V}{1+q\Delta V/V}\right)(1+Bp+Cp^2) \tag{7}$$

or in the limit $p=0$:

$$\frac{1}{\lambda}\frac{d\lambda}{dp} = (q-\tfrac{1}{3})\kappa + \left(\frac{dR}{dT}\right)^{-1}\frac{d^2R}{dTdP} \ . \tag{8}$$

IV. RESULTS FOR λ(p)

In this section we obtain results for $\lambda(p)$ based on Eq. (7), published values for the compressibility and our measurements of the pressure dependence of $d\rho/dT$. In order to compare these results with experiments the calculated $\lambda(p)$ is inserted into McMillan's formula[3]

$$T_c = \frac{\Theta}{1.45}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right] \tag{9}$$

and compared with experimental results for $T_c(p)$. This is a convenient and presumably reliable check on the expressions for $\lambda(p)$.

In order to calculate $T_c(p)$ we first perform a standard calculation with the advantage of being simple and general. Three simplifying assumptions enter this calculation. (i) $q=1$ in Eq. (7). It should be noted that this is somewhat more general than an assumption of free electrons and implies that the plasma frequency scales with pressure as in the free-electron model. (ii) The pressure dependence of the Debye temperature $\Theta(p)$ is given by

$$\Theta(p) = \Theta(0)(1+\gamma_G\kappa p) \ , \tag{10}$$

where γ_G is the room-temperature Grüneisen parameter. (iii) The Coulomb pseudopotential μ^* is independent of pressure and spin fluctuations and their pressure dependence (presumably relevant only for V) are not considered. Then, in the next section, we discuss these simplifying assumptions and the consequences for the different elements of more detailed considerations.

In all cases γ_G is taken from Table III and the data for $\Delta V(p)/V(0)$ from Vaidya and Kennedy.[10,11] In the numerical expressions below p is always in GPa.

A. Sn

From tunneling results[16] $\lambda(0)=0.72$ and $\mu^*=0.092$ are obtained. To scale with the observed zero-pressure result for T_c in the apparently most accurate pressure experiments[17] we take $\Theta(0)=114$ K in Eq. (10). In the modification of the McMillan equation introduced by Dynes[18] $\Theta/1.45$ is replaced by $\langle\omega\rangle/1.20$ where $\langle\omega\rangle$ is a suitably averaged phonon frequency. The value of 114 K used here agrees reasonably with $1.45\langle\omega\rangle/1.20 = 133$ K obtained from tunneling experiments.[16] The results are

$$\lambda(p) = 0.72(1-0.0825p+0.0055p^2) \tag{11}$$

and

$$\Theta(p) = 114(1+0.040p) \tag{12}$$

expressed in (K).

The result for T_c is shown in Fig. 3. The calculat-

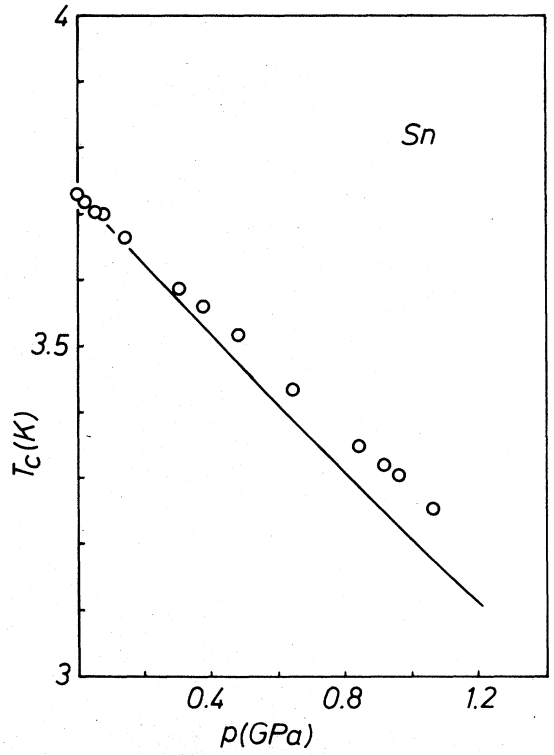

FIG. 3. T_c vs p for Sn. The curve is calculated from Eqs. (9), (11), and (12). The points are the experiments of Ref. 17.

ed curve gives the correct initial slope $dT_c/dp_{p=0}$ but decreases somewhat faster than the experimental results at pressures above about 0.3 GPa. It can be noted however that Wittig's result[19] at 4.7 GPa with $T_c \sim 1.9$ K is close to the result calculated from Eqs. (9), (11), and (12). Due to the sensitivity of the term in p^2 in Eq. (11) to C in Eq. (7) and to higher-order terms in $\Delta V/V$ and the uncertainty in both of these quantities this agreement may be fortuitous.

B. Pb

There are several measurements of the resistance of Pb under pressure by Bridgman. In one set of experiments[13,14] the average pressure coefficient of resistance to about 0.7 GPa was determined at a few widely separated temperatures. These measurements are therefore suitable to determine $d\rho/dp$ as a function of T from which the required derivative $d^2\rho/dTdp$ can be obtained and $\lambda(p)$ calculated. The result is[20]

$$\lambda(p) = 1.55(1 - 0.115p) \tag{13}$$

with $\lambda(0) = 1.55$ from tunneling results.[16]

In a second experiment Bridgman measured $\Delta R/R$ at 30 and 75 °C as a function of pressure up to 3 GPa.[21] These results thus give $(d\rho/dT)(p)$ from which $\lambda(p)$ can be determined from Eq. (7). We obtain

$$\lambda(p) = 1.55(1 - 0.1334p + 0.0096p^2) \ . \tag{14}$$

From tunneling experiments[16] $\mu^* = 0.105$. $\Theta(0) = 75$ K then gives the correct zero-pressure value for T_c in Eq. (9) and is also in agreement with $1.45\langle\omega\rangle/1.20 = 73$ K from tunneling results.[16] Further

$$\Theta(p) = 75(1 + 0.066p) \tag{15}$$

in K.

The results for T_c calculated from both Eq. (13) as well as Eq. (14) are shown in Fig. 4 together with experimental results[19,22–25] from several sources. Within the pressure range shown the agreement with experiments is quite satisfactory. At higher pressures, above 2.5 GPa, the calculated T_c is lower than the values observed by Eichler and Wittig.[26]

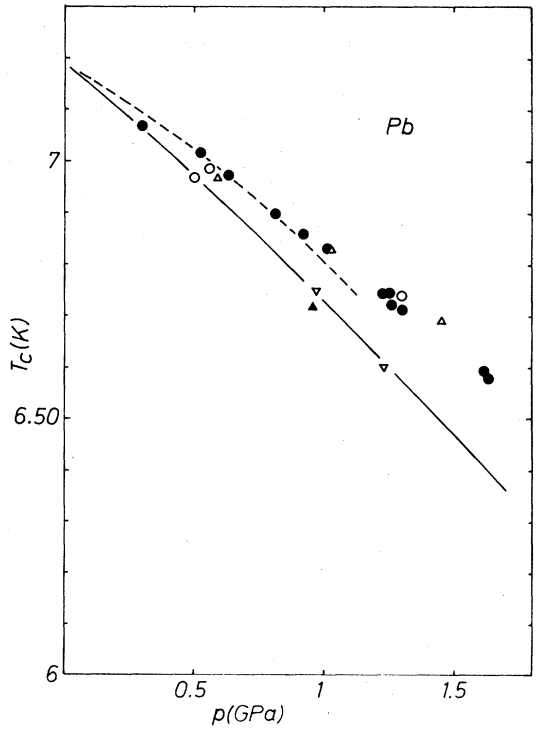

FIG. 4. T_c vs p for Pb. The dashed curve is calculated from Eqs. (9), (13), and (15), the full curve from Eqs. (9), (14), and (15). The experimental points are from: ▲ Ref. 22; ▽ Ref. 19; Δ Ref. 23; ○ Ref. 24; and ● Ref. 25.

C. Al

$T_c(p)$ for Al was previously calculated[2] from our resistivity measurements taking $q=0$ in Eq. (7). These results show excellent agreement with the experiments up to 4 GPa. For comparison with our present standard approximation we here calculate $\lambda(p)$ with $q=1$ and obtain

$$\lambda(p)=0.39(1-0.0341p+0.0012p^2) \quad . \tag{16}$$

This expression overestimates the observed $T_c(p)$ somewhat. In the region up to 1.5 GPa the discrepancy is of the same magnitude as that for Sn (Fig. 3).

D. Zr

The small value of B of Eq. (1) for Zr causes the volume term of Eq. (7) to dominate and $\lambda(p)$ increases with pressure. With[3] $\lambda(0)=0.41$, $\mu^*=0.13$, and $\Theta(0)=290$ K we obtain

$$\lambda(p)=0.41(1+0.0029p) \tag{17}$$

and

$$\Theta(p)=290(1+0.0080p) \tag{18}$$

again in (K). T_c versus pressure calculated from these expressions is shown in Fig. 5. To compare

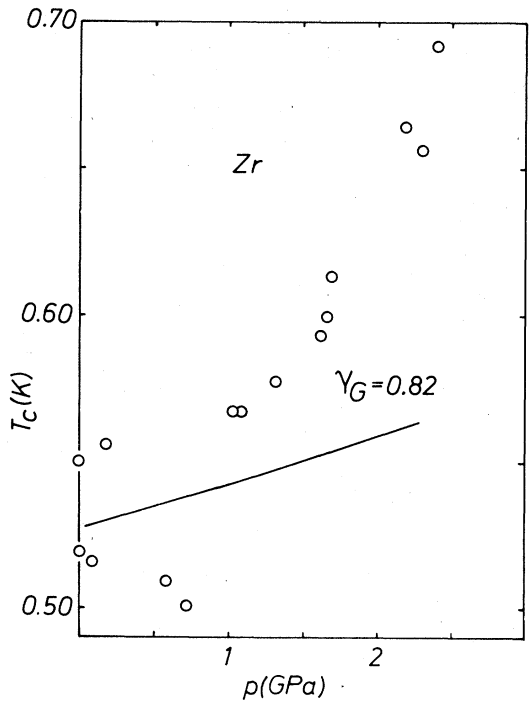

FIG. 5. T_c vs p for Zr. The curve is calculated from Eqs. (9), (17), and (18). The experimental points are from Ref. 27.

with experiments we have chosen the data of Brandt and Ginzburg[27] for their unannealed samples which would correspond to the condition of our sample. The experimental data are scattered, presumably reflecting the experimental difficulties. Although the overall increase with pressure of the observed T_c is much stronger than that obtained from resistivity it is satisfying to observe that the calculated curve has the right sign of dT_c/dp and possibly also the correct magnitude at $p=0$.

E. dhcp La

Although the pressure coefficient of resistivity is numerically larger in La than in Zr the compressibility is much larger and again $\lambda(p)$ increases with pressure:

$$\lambda(p)=0.85(1+0.019p) \quad . \tag{19}$$

Here $\lambda(0)$ is calculated from Eq. (9) with $\mu^*=0.13$, $\Theta=142$ K from the low-temperature specific heat[12] and the presently observed T_c. Further

$$\Theta(p)=142(1+0.028p) \tag{20}$$

in K which with Eq. (19) gives an average dT_c/dp in the interval 0–1 GPa of +0.4 K/GPa. Although this result has the correct sign it is smaller than most experimental results in the literature. The best results are probably those by Maple *et al.*[4] of +1.3 K/GPa. Smith and Gardner[5] obtain +1.9 K/GPa. Rohrer,[28] on the other hand, gives a value of only +0.1 K/GPa.

F. V

From McMillan[3] we take $\lambda(0)=0.60$, $\mu^*=0.13$, and $\Theta(0)=400$ K and obtain

$$\lambda(p)=0.60(1-0.0114p) \tag{21}$$

and

$$\Theta(p)=400(1+0.012p) \tag{22}$$

in K. The average dT_c/dp in the region up to 1 GPa is then found to be −0.16 K/GPa. The earlier controversies about the experimental T_c versus p in V seem to have been settled by Smith[29] who gives for dT_c/dp +0.062 K/GPa. Our simplified approach to the calculated dT_c/dp thus fails to give the correct sign in this case. The absolute deviation, however, is only 0.2 K/GPa.

V. DISCUSSION

The results show that the pressure dependence of $d\rho/dT$ at a high temperature accounts satisfactorily

for $\lambda(p)$ for the simple metals (Sn, Pb, Al), while the same approach is, at the very best, only qualitatively correct for the transition metals (Zr, La, V). The reason for this can be understood from Table III. For the nontransition metals the pressure coefficient of resistance is larger than the compressibility and dominates in the pressure dependence of λ. In contrast, for the transition metals the compressibility is relatively larger and therefore the pressure dependence of the plasma frequency, described by the parameter q of Eq. (5), is important in determining $\lambda(p)$.

A. Pressure dependence of ω_p

We now combine results from the literature on the pressure dependence of T_c with our resistivity measurements under pressure and calculate from Eqs. (7), (9), and (10) the value of q which brings the calculated $T_c(p)$ into agreement with the experiments. The results are given in Table IV.

For Pb the experimental data for $d\rho/dT$ as well as T_c (Fig. 4) are too scattered to enable q to be determined. For Al the value $q=0$ was shown previously[2] to give excellent agreement between the calculated and observed T_c:s. For Zr we calculate the value of q which yields the slope, $dT_c/dp=0.09$ K/GPa, quoted for the unannealed samples in the original experiments.[27] For Sn, La, and V the q values given are those for which the calculated T_c:s agree with the experiments[4,17,29] at 1 GPa.

It is not surprising that the numbers for q in Table IV deviate from unity. In fact, already in Al the different signs of the pressure dependence of different averages of the electron velocities[30] clearly illustrate the breakdown of free-electron-like scaling. For the elements presently studied we have found relevant information on ω_p only for (i) Al and (ii) La, and in both cases there is an encouraging agreement with the estimates in Table IV. Claesson and Larsson[31] calculate the pressure dependence of ω_p for Al and find it to be essentially independent of pressure. (ii) There is a recent calculation[32] for fcc La. Recalling that our $N(\epsilon_F)$ is taken per unit volume of crystal we calculate from these data an average value of about $q=3.5$ for pressures up to ~ 10 GPa. This value is not directly comparable to that in Table IV as it refers to a different crystal structure but its magnitude indicates that the result for dhcp La is reasonable.

TABLE IV. The pressure dependence of the plasma frequency [q is defined in Eq. (5)].

Element	Sn	Al	Zr	La	V
q	1.4	0	2.8	2.9	2.6

B. Phonon structure

To describe the phonon properties under pressure the quantity presently of interest is $\gamma=-d\ln\langle\omega\rangle/d\ln V$. This is not readily available and in Eq. (10) we have followed the customary approach and replaced γ by the usual Grüneisen

$$\gamma_G=-\left(\sum C_i d\ln\omega_i/d\ln V\right)\Big/\sum C_i \ ,$$

where ω_i and C_i are the frequency and specific-heat contribution, respectively, for the mode i and γ_G is evaluated at room temperature. Obviously the modes are weighted quite differently in γ_G. What are the expected corrections to this approach?

To illustrate this problem we compare in Table V γ_G from Table III with the Grüneisen constants for the elastic limit, γ_{GE}, derived from (room-temperature) compressibility measurements.[10–12,33] γ_{GE} contains the ratio of the coefficients in the power-series expansion of $V(p)/V(0)$ which may be rather uncertain and the data from different sources show some scatter. It is seen, however, that for the nontransition metals the pressure shifts of the long-wavelength phonons are overestimated by γ_G while for the transition metals presently studied the corresponding shifts are underestimated by γ_G. For the nontransition metals these differences are of minor significance in $T_c(p)$ due, again, to the strong pressure dependence of $d\rho/dT$. For the transition metals there is a clear trend for larger differences between γ_G and γ_{GE} and furthermore $d\rho/dT$ depends only weakly on pressure. Therefore corrections to Eq. (10) would be significant only for these metals.

As γ_{GE} is larger than γ_G for the transition metals the correction to the calculated dT_c/dp is positive. We can drastically overestimate this effect by replacing γ_G in Eq. (10) by γ_{GE}. It is then found that for La and V there are only small changes in the calculated $T_c(p)$. For Zr, on the other hand, there are significant changes in dT_c/dp and the corrections to Eq. (10) may thus be significant.

The conclusion that Eq. (10) is generally adequate when calculating dT_c/dp is in agreement with empirical estimates.[34] The conjecture that this is expected as long as there are no temperature-dependent soft-phonon modes[35] again singles out Zr, where the shear modes show an unusual softening.[36] Also in La softening is apparent from the low-energy part of the tunneling phonon spectrum.[37]

Summarizing this discussion we thus find that, among the elements studied, corrections to Eq. (10)

TABLE V. Ratio of elastic to specific-heat Grüneisen parameters: γ_{GE}/γ_G.

Source	Sn	Pb	Al	Zr	La	V
a	0.86	0.54	0.95	3.2	2.0	1.4
b	0.85	0.61	0.67	1.8	1.8	3.9
c				8.4		

[a]Bridgman as compiled by Gschneidner (Ref. 12).
[b]Calculated from Vaidya and Kennedy (Refs. 10 and 11).
[c]Calculated from Olinger and Jamieson (Ref. 33).

are significant for, at most, Zr and La implying possible positive contributions to dT_c/dp. The estimates of the pressure dependence of ω_p in Table IV should therefore be regarded as upper limits for these metals.

We also mention the possibility that the anomalous pressure and temperature dependence of a soft-phonon mode would invalidate the assumed equality $d\lambda/dp = d\lambda_{tr}/dp$. La with its unusual phonon properties[37] could be one example.

C. μ^* and spin fluctuations

The pressure dependence of the Coulomb pseudopotential μ^* is generally believed to be small.[38–40] Our previous results for Al confirm this.[2] These results generally refer to nontransition metals but similar conclusions are obtained for the transition metals. With[41]

$$\mu^* = \mu/[1 + \mu \ln(\epsilon_F/k_B\Theta)] \ , \tag{23}$$

where μ is the screened Coulomb interaction, Smith[29] treated μ in the Thomas-Fermi approximation and derived $d\ln\mu^*/d\ln V \sim 0.3\gamma_e$ where γ_e is the electronic Grüneisen parameter. In Zr, where[42] the experimental $\gamma_e \sim 0$ this effect is thus negligible. For V we take an upper limit of[43] $\gamma_e \simeq 2$ which gives a value for $d\ln\mu^*/dp$ which is three times larger than an early estimate by Garland and Benneman[34] but nevertheless implies a negligible correction to our calculated $T_c(p)$. The effect is small also in La although here, surprisingly, a negative sign of $d\ln\mu^*/d\ln V$ is expected from this estimate.[43] Therefore, in all of the presently studied metals, it seems justified to disregard the pressure dependence of μ^*.

We also briefly mention the role of spin fluctuations on $T_c(p)$. Such excitations have long been assumed to exist in the early transition metals although usually considered to be small.[34] In V, however, an estimate of the contribution of spin fluctuations to the electron specific-heat mass enhancement, λ_{sp}, as high as 0.38 was obtained[44] and the magnitude of such a value was recently independently confirmed.[45] Such a large value changes the derivative of T_c with respect to the various parameters in Eq. (9) and the pressure dependence of λ_{sp} should be taken into account when $T_c(p)$ is calculated.

From the broadening of the electron bands under pressure λ_{sp} is expected to decrease with p and thus give a correction to the calculated T_c which increases with pressure. It is difficult however to estimate the magnitude of this effect. An early qualitative estimate[34] yields for vanadium $d\ln\lambda_{sp}/d\ln V \simeq 2.5$ which has some influence on the calculated dT_c/dp. If we account for the possibility that the pressure dependence of λ_{sp} has a non-negligible influence on $T_c(p)$ the value of q in Table IV for V should be regarded as an upper limit.

VI. CONCLUDING REMARKS

The main results of the present paper are twofold. (i) Accurate data are presented for the resistance of Sn, Zr, dhcp La, and V as a function of temperature and pressure. We analyze these data in the form of a series expansion from a fixed temperature and pressure and obtain expressions for $R(p,T)$ with a precision of a few parts in 10^{-4}. (ii) From these data we obtain the pressure dependence of $d\rho/dT$ which is found to be a useful parameter in the description of the superconducting T_c under pressure.

In fact for the nontransition metals studied (Sn, Pb, Al) the relative pressure dependence of $d\rho/dT$ is much stronger than the compressibility and dominates in the calculation of the pressure dependence of λ. These results show that $\lambda(p)$ is measured up to 1 GPa by the pressure dependence of $d\rho/dT$ to a precision of about 5% for Sn and to better than 3% for Al.

For the transition metals (Zr, La, V) the pressure dependence of T_c is, at the very best, qualitatively correct when it is calculated from the pressure dependence of $d\rho/dT$ and an assumed free-electron-like scaling of the energy bands. This is due to the relatively small pressure dependence of $d\rho/dT$ in these metals which implies that the calculated T_c is much

more sensitive to the compressibility, the plasma frequency and the correct choice of a Grüneisen γ. It is well known in the literature that $T_c(p)$ for transition metals can be looked upon as a delicate balance between factors of opposite pressure dependences. By using the pressure dependence of $d\rho/dT$ as a new measurable parameter we obtain a description of this balance [Eqs. (7) and (10)] which, compared to some other formalisms,[34,46] contains a relatively small number of physically transparent parameters.

Thus, by combining results for the pressure dependence of T_c and $d\rho/dT$, estimates of the pressure dependence of the plasma frequency are obtained. Results for this quantity are scarce in the literature. Published band-structure calculations, however, support our results for Al and La. The influence of phonon properties and spin fluctuations on these estimates is discussed. In summary this influence is small except, perhaps, in a few specified cases. The estimates of the pressure dependence of the plasma frequency should therefore be taken as upper limits for the transition metals.

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