J. Phys. F: Metal Phys., 1971, Vol. 1. Printed in Great Britain

Effects of pressure on superconducting properties of simple metals†

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MS. received 25th *September* 1970

Abstract. First principles studies of the superconducting behaviour under pressure of the simple metals Al and Pb have been made. Good agreement is obtained with the experimental volume derivative of the transition temperature in Al and, for higher compressions, upward deviations are predicted to occur from the linear relationship with volume observed at low pressures. In Pb, the relative rates of decrease under pressure of T_c, Δ_0, and $2\Delta_0/k_BT_c$ show the same trends as experiment, while in Al the ratio $2\Delta_0/k_BT_c$ is found not to vary significantly with compression.

1. Introduction

The superconductivity of simple metals is now understood theoretically to high precision (see, for instance, Parks 1969). In this paper we calculate the pressure dependence of the superconducting parameters of Al and Pb and assess the extent to which quantitative first principles calculations of transition temperatures are now possible.

Many experimental studies of the effects of pressure on superconductivity have been made in the last fifteen years, and the results for simple metals have been summarized by Smith and Chu (1967). They showed that, over the range of pressures so far covered, the transition temperatures, T_c, of simple metals decrease linearly with volume, Ω. In Al, the measurements extend to compressions of almost 3%, for which T_c is decreased by 40%, and in Pb a decrease of 50% is found for the maximum compression of 20%. Extrapolating these curves, they predicted the eventual suppression of superconductivity by pressure. In addition, it has been found (Franck and Keeler 1968, Galkin and Svistunov 1968) that in Pb the ratio $2\Delta_0/k_BT_c$ decreases under pressure at about the same rate as does T_c itself. The relative experimental pressure derivatives are included in table 1.

The most detailed calculations of the superconducting properties of metals that have been performed to date are those of Carbotte and Dynes (1968). They calculated electron–phonon coupling functions from the model electron–ion potentials of Animalu and Heine (1965, to be referred to as AH) and experimental phonon dispersion curves, and thence the zero temperature energy gap at the gap edge, Δ_0, from the strong coupling theory of superconductivity. These calculations were extended to variable volume by Trofimenkoff and Carbotte (1969, 1970) by scaling the phonon frequencies by the measured change in sound velocities and rescreening the potential. They obtained good agreement with experimental values of Δ_0, T_c and their volume derivatives for both Al and Pb.

We have shown (Coulthard 1970, to be referred to as I) that local AH potentials can be used to predict quite reliably the phonon frequencies and their pressure derivatives in the simple metals Na, K and Al, but that the calculations are not adequate for Pb. Dynamic electron–phonon coupling functions $\alpha^2(\nu)F(\nu)$ calculated from these potentials and frequencies have also been found to be satisfactory (Coulthard 1971, preceding paper, to be referred to as II). This then suggests that a semi-quantitative explanation of the observed superconducting behaviour of Al under pressure can be given, without recourse to other experimental data, by using these coupling functions in the strong coupling theory. While

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Table 1. Calculated pressure dependence of Δ_0 and T_c in Pb

Compression (%)	λ	T_c	Δ_0	$\frac{2\Delta_0}{k_B T_c}$
0	1·71	7·19	1·35	4·34
5	1·50	6·65	1·19	4·14
$-\frac{d \ln X}{dP}$ (10^{-6} bar^{-1})	calc.[a]	3·7	5·8	2·3
	expt.[b]	$4·9 \pm 0·2$	$10·1 \pm 0·8$	$5·2 \pm 0·6$

[a] Pressure derivatives (for bulk metal) obtained from volume dependence via P–Ω equation of Munson and Barker (1966).

[b] Franck and Keeler (1968); thin film.

similar calculations in Pb can indicate only the trends of T_c and Δ_0, the difference in their volume derivatives is most likely associated just with the greater strength of the electron–phonon coupling and should therefore be apparent even if the calculation of the coupling is approximate. Our results confirm these expectations.

2. Theory and calculation procedure

The strong coupling theory of superconductivity in simple metals is well known (Schrieffer 1964) so we just review the resulting gap equations here. The electron–phonon interaction is treated, according to the analogue for superconductors of Migdal's (1958) approximation, to $O(m/M)^{1/2}$, where m and M are the electron and ion masses respectively, and the Coulomb interactions between electrons are also included. Anisotropies in the electron self-energy, which arise from those in the electron–phonon interaction, band structure, and phonon density of states, are relatively small in the simple metals (Bennett 1965). Averaging over these, equations for the renormalization function $Z(\omega)$ and the gap function $\Delta(\omega)$ at the Fermi surface are obtained. At zero temperature, these are

$$\{1 - Z(\omega)\}\omega = \int_{\Delta_0}^{\infty} d\omega' \, \mathrm{Re}\left[\frac{\omega'}{\{\omega'^2 - \Delta^2(\omega')\}^{1/2}}\right] K_-(\omega, \omega')$$

$$\Delta(\omega) = \frac{1}{Z(\omega)} \int_{\Delta_0}^{\infty} d\omega' \, \mathrm{Re}\left[\frac{\Delta(\omega')}{\{\omega'^2 - \Delta^2(\omega')\}^{1/2}}\right] \{K_+(\omega, \omega') - \mu^* \theta(\omega_c - \omega')\} \qquad (1)$$

where $\mathrm{Im}\,[Z(\omega)\{\omega^2 - \Delta^2(\omega)\}^{1/2}] > 0$,

$$K_\pm(\omega, \omega') = \int_0^{\infty} d\nu \, \alpha^2(\nu) F(\nu) \left(\frac{1}{\omega' + \omega + \nu + i\delta} \pm \frac{1}{\omega' - \omega + \nu - i\delta}\right)$$

and $\alpha^2(\nu) F(\nu)$ is the effective electron–phonon coupling function defined in equation (1) of II. The electron–electron Coulomb pseudopotential μ^* has the form (Schrieffer 1964)

$$\mu^* = \frac{N(0)V}{1 + N(0)V \ln(\epsilon_F/\omega_c)} \qquad (2)$$

where V is an average over the Fermi surface of the screened Coulomb interaction between electrons, $N(0)$ is the electron density of states at the Fermi surface, excluding electron–phonon renormalization effects, and ω_c is a cut-off frequency of order $5\omega_D$, where ω_D is the Debye energy. As in II, we neglect the Coulomb vertex corrections and quasi-particle renormalization factors in $\alpha^2(\nu) F(\nu)$ and μ^*.

The gap equations at nonzero temperature are more complicated than (1) but have the same general form (Scalapino *et al.* 1965), so we will not give them here. The gap edge at temperature T, Δ_T, is defined by

$$\Delta_T = \mathrm{Re}\,\Delta(\omega = \Delta_T) \qquad (3)$$

and vanishes at the superconducting transition temperature. A semi-empirical formula for T_c has been obtained by McMillan (1968) using the strong coupling gap equations:

$$T_c = \frac{\theta_D}{1{\cdot}45} \exp\left\{\frac{-1{\cdot}04(1+\lambda)}{\lambda - \mu'(1+0{\cdot}62\lambda)}\right\} \tag{4}$$

where θ_D is the Debye temperature and λ the electron–phonon coupling strength defined in equation (2) of II; μ' is given by equation (2) above with $\omega_c = \omega_D$.

The calculation of the $\alpha^2(v)\,F(v)$ functions has been discussed in II. Phonon frequencies along the principal symmetry directions are calculated (see I) from a local AH model potential screened by the dielectric function of Shaw and Pynn (1969), and off-symmetry frequencies generated by a Kubic harmonic fit to these. The phonon polarization vectors are treated in an isotropic approximation and a one-orthogonalized plane wave matrix element used for the electron–phonon interaction. The pseudopotential μ^* has been calculated for both Thomas–Fermi and random phase approximations to the screened electron–electron Coulomb interaction.

An estimate of T_c can be obtained from McMillan's formula (4), but it does not provide a value of Δ_0 as well and so allow a study of the variation of the ratio of these quantities. The applicability of the formula is also somewhat restricted because the calculations on which it was based were performed for a fixed shape of $\alpha^2(v)F(v)$ and because it may not be reliable for very strong coupling metals such as Pb (McMillan 1968, Chen *et al.* 1969). We have therefore used this formula for predicting qualitative trends, but have also obtained Δ_0 and T_c as functions of pressure by solving the gap equations in detail.

Given values for $\alpha^2(v)\,F(v)$ and μ^*, the zero temperature gap equations (1) are readily solved by iteration and the gap edge Δ_0 determined from equation (3). For $T \sim T_c$, we have $\Delta(\omega') \sim 0$ so that the gap equations can be linearized, and again solved iteratively. As these equations are now only strictly valid for $T = T_c$, the transition temperature is found by seeking that temperature at which the iterations for $\Delta(\omega)$ are exactly convergent. Apart from possible systematic errors of up to $\pm$ 5% in T_c in Al, the numerical accuracy of our results for the superconducting properties is believed to be better than $\pm$ 1%.

3. Results and discussion

We first summarize the results of our calculation in II of the volume dependence of the electron–phonon coupling and discuss the calculation of the Coulomb pseudopotential. The corresponding changes in the superconducting properties of the metals are then studied and compared with experiment and with previous calculations.

3.1. *Electron–phonon and electron–electron interactions*

Although our method of calculation of the electron–phonon coupling $\alpha^2(v)F(v)$ and λ from given phonon frequencies and model potential is quite reliable, uncertainties in the theoretical potential, errors in the phonon dispersion curves calculated from them and so on imply an uncertainty of perhaps 20% in λ. For a fixed form of potential such systematic errors matter less, so that the calculated volume dependence of λ should be reliable as that of the phonons. Thus our results for Al, which are shown in figure 1, should be at least qualitatively accurate. The calculations for Pb underestimate the volume derivative of λ.

The Coulomb pseudopotential μ^* is slightly dependent upon the approximation used for the screened electron–electron interaction but the errors involved are considerably less than the uncertainties in our calculated values of λ. For each metal we neglect the slow decrease of μ^* with volume which, as can be seen from the results for Al in figure 1, is much less important than that of λ.

3.2. *Superconducting properties*

Points of reference for the solution of the superconducting gap equations are provided by using previously determined values of $\alpha^2(v)\,F(v)$. From McMillan and Rowell's (1965,

1969) experimental results for Pb, which were determined from effectively zero temperature tunnelling data, we find $\Delta_0 = 1{\cdot}34$ meV, $T_c = 7{\cdot}33$ K, and $2\Delta_0/k_B T_c = 4{\cdot}23$. The agreement of the last two quantities with experiment (Adler *et al.* 1967, Franck and Keeler 1967) indicates that the strong coupling gap equations give a consistent description of the superconducting properties of Pb at all temperatures, and provides a check on our numerical work. Similarly we find, from Carbotte and Dynes' (1968) calculated values of $\alpha^2(v)F(v)$ for Al, $\Delta_0 = 0{\cdot}188$ meV, $T_c = 1{\cdot}27$ K and $2\Delta_0/k_B T_c = 3{\cdot}44$. As we mentioned in § 2, there may be systematic numerical errors of up to 5% in T_c for Al. The calculated ratio of Δ_0 to T_c agrees reasonably with the BCS value of 3·52, as we would expect for this weak coupling superconductor, and also with experiment (Blackford and March 1968).

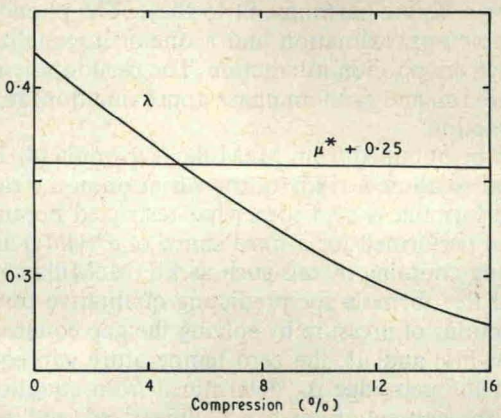

Figure 1. Volume dependence of calculated effective electron–phonon (λ) and Coulomb (μ^*) coupling strengths in Al.

We now turn to the results obtained with our calculated coupling functions. When the coupling strength is small, uncertainties in λ and μ^* imply large variations in the predicted T_c, as can be seen from equation (4). In Na, Shaw's potential provides the best description of the lattice dynamics (see I) and also the larger value of λ (II). Using our calculated μ^* of 0·13, we find $T_c < 10^{-4}$ K, but Allen and Cohen (1969) suggest that $\mu^* = 0{\cdot}16$ is a better estimate. Superconductivity is even less likely in *K* and, as λ decreases with volume, compression further lowers the probability of its occurrence in either.

As the transition temperature in Al is also quite sensitive to errors in the coupling constants, we first adjusted μ' from 0·105 to 0·12 so that McMillan's formula (4) yielded the measured transition temperature of 1·2 K at zero pressure. The volume dependence of T_c was then calculated from the values of λ in figure 1, and is shown in figure 2. The linear fit to the experimental points (Smith and Chu 1967) is also given and the agreement is seen to be reasonable. As with the phonon frequencies and elastic constants (see I), the theoretical pressure derivative is somewhat smaller than experiment. Upward deviations from linearity are evident in the theoretical curve beyond about 2% compression.

To verify these results, and also to study the behaviour of Δ_0, we have performed explicit calculations of T_c and Δ_0, using unadjusted values of μ^*, at compressions of 0, 2 and 4%. At zero pressure these yield $T_c = 1{\cdot}35$ K, $\Delta_0 = 0{\cdot}196$ meV and $2\Delta_0/k_B T_c = 3{\cdot}36$. In view of the errors and uncertainties in λ, this agreement with experiment is fortuitous. McMillan's formula yields $T_c = 2{\cdot}00$ K for the corresponding parameters, which partly reflects the limitations of equation (4) discussed above. The value of $2\Delta_0/k_B T_c$ agrees closely with that calculated from Carbotte and Dynes' $\alpha^2(v)\,F(v)$. For the finite compressions, this ratio changed by less than $\pm$ 0·01, while the values of Δ_0 and T_c continued to show nonlinear behaviour (see figure 2). The initial slope yields

$$\frac{\mathrm{d}\ln T_c}{\mathrm{d}\ln \Omega} = 14 \qquad \text{and} \qquad \frac{\mathrm{d}\ln T_c}{\mathrm{d}P} = -18 \times 10^{-6}\,\mathrm{bar}^{-1}$$

where we have used the P–Ω relation of Munson and Barker (1966), compared with the experimental values of 16 and -21 respectively in the same units (Smith and Chu 1967). In our approximate calculation by Hodder's (1969) technique in I, using a Lorentzian model for $\alpha^2(\nu)\,F(\nu)$, McMillan's formula (4) and the calculated pressure derivatives of the maximum phonon frequencies, we fortuitously obtained $\mathrm{d}\ln T_c/\mathrm{d}P = -20 \times 10^{-6}\ \mathrm{bar}^{-1}$ for Al. In subsequent calculations (Coulthard, Ph.D. thesis, University of London 1969,

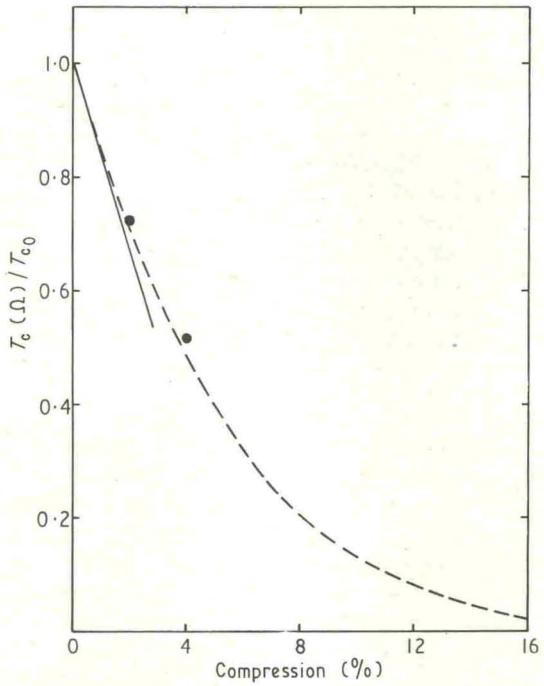

Figure 2. Volume dependence of transition temperature in Al. The full curve is the linear fit to the experimental points (Smith and Chu 1967). The broken curve is the calculation with McMillan's formula, for which $T_{c_0} = 1{\cdot}23$ K. The dots were obtained by direct solution of the gap equations with $\Delta_0 = 0{\cdot}196$ meV and $T_{c_0} = 1{\cdot}35$ K. For both $\lambda_0 = 0{\cdot}42$ while μ^* and $\mu' = 0{\cdot}12$.

unpublished) the integral for $\alpha^2(\nu)\,F(\nu)$ was simplified to one dimension by spherical averaging, but the volume dependence of λ was much the same as we found in II and we obtained $\mathrm{d}\ln T_c/\mathrm{d}P = -14{\cdot}5 \times 10^{-6}\ \mathrm{bar}^{-1}$ in Al. The errors in that and in the current results are due partly to those in the phonon pressure derivatives and partly to the fact that our calculated zero pressure transition temperatures were somewhat larger than the experimental value. Calculations with variable normalizations for λ and μ^* indicate that the logarithmic derivative of T_c will increase as T_c decreases. Therefore, once the zero pressure transition temperature is predicted correctly, we would expect the pressure derivative to agree quite well with experiment, as has been found by Trofimenkoff and Carbotte (1969).

The corresponding results for Pb are given in table 1. To reproduce the experimental zero pressure transition temperature of 7·2 K using McMillan's formula, we renormalized λ to 1·2, in good agreement with McMillan's (1968) empirical value, but considerably smaller than the directly measured value of 1·53 (Franck *et al.* 1969). The initial slope of the $T_c(\Omega)$ curve is then 20% larger than experiment, but this is partly due to the artificially small values of λ used. Small upward deviations from linearity are only evident for compressions of about 20%, for which the transition temperature has again been halved.

Direct solution of the gap equations using the calculated values of λ yields qualitative agreement with experiment, as can be seen in table 1. In particular, we note that the initial fractional change in Δ_0 is much larger than that in T_c, as found experimentally (Franck and Keeler 1968). That Pb, on compression, tends to behave more like a BCS superconductor is readily apparent from the sharp decrease in the ratio of Δ_0 to T_c. As with Al, these results differ little from those we obtained using a spherical averaging approximation in the coupling function, indicating that only the average effects of compression are of importance here.

Similar results for Pb and Hg were obtained by Trofimenkoff and Carbotte (1970) by rescaling the experimental $\alpha^2(\nu)F(\nu)$ using average experimental Gruneisen constants and rescreening of the AH potentials, as well as with first principles calculations of $\alpha^2(\nu)F(\nu)$ from experimental phonons and their pressure derivatives. This all confirms the average nature of the effect. For Al, they (1969) found an upward deviation from linearity in their $\Delta_0(\Omega)$ values for a compression of 5%. Calculations by Seiden (1969) and Kakitani (1969), using model forms for the electron–phonon interaction and McMillan's form of equation for T_c, have both predicted similar deviations from linear decrease with volume, but in all cases T_c was eventually pushed below presently measurable temperatures. We have obtained much the same results here in fully theoretical calculations of phonon frequencies, coupling functions and superconducting parameters.

4. Conclusions

As we discussed in II, the uncertainty in the electron–phonon coupling function arising from those in the screened model potential is considerable. By a serendipitous choice of potential and dielectric function from the many now available, one can obtain agreement with most experimental results, but reliable quantitative first principles calculations of superconducting transition temperatures are not possible at present. For instance, an error of 5% in λ in Al implies about a 20% change in T_c. However, the behaviour of simple metal superconductors as one parameter is varied may be accounted for. We have shown here that detailed calculations of $\alpha^2(\nu)\,F(\nu)$ can be used, in the strong coupling gap equations, to provide a qualitative first principles theoretical explanation of the observed changes under pressure of the superconducting parameters Δ_0 and T_c in Al and Pb. Going beyond the present range of experiments, our calculations predict that upward deviations will occur from the observed linear decrease of T_c with volume, but that superconductivity will probably still be eventually depressed below measurable temperatures. In the weak coupling superconductor Al the ratio of Δ_0 to T_c is found not to change with compression.

From our results in this series of papers we expect that, given a representation of the screened electron–ion potential that can account for the phonon dispersion curves of a particular simple metal, the strong coupling theory should then lead to a quantitative understanding of its superconducting properties. The success of Allen and Cohen (1969) in predicting transition temperatures for the hcp metals Zn and Cd using empirical pseudopotentials extracted from extensive Fermi surface data tends to confirm this expectation. The Coulomb vertex and renormalization corrections we mentioned in § 2 would have to be included in such calculations, as would higher order band structure corrections to $\alpha^2(\nu)\,F(\nu)$. However, the theoretical potentials available now are not sufficiently reliable for this to be meaningful.

Acknowledgments

I would like to thank Dr S. Doniach for suggesting this problem and both him and Dr M. J. Zuckermann for their supervision and guidance of the work. Discussions of the manuscript with Dr D. J. W. Geldart have also been most helpful. The financial support of an Exhibition of 1851 Overseas Scholarship is gratefully acknowledged, as is that of a National Research Council of Canada Post-Doctoral Fellowship while the work was being completed.

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