

# MASTER

CONF-790653--4

## PROGRESS IN CALCULATIONS OF THE SUPERCONDUCTING PROPERTIES OF TRANSITION METALS<sup>1</sup>

W. H. Butler

Metals and Ceramics Division  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee

NOTICE  
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

*First principles calculations of the electron-phonon parameters of d-band metals can now be performed to an accuracy of about 10% for "averaged" quantities such as the mass enhancement or the room temperature resistivity. Quantities such as the spectral function  $\alpha^2F(\omega)$  or the phonon linewidth which describe the electron-phonon interaction in more detail can also be calculated. Agreement between calculated and experimental phonon linewidths is generally good but there are differences between the experimental and calculated versions of  $\alpha^2F(\omega)$ . Calculations of the thermodynamic critical field and the upper critical field for Nb agree well with experiment.*

### I. TECHNIQUES

The two basic techniques which have been used in calculating electron-phonon parameters are the rigid-muffin-tin approximation (RMTA) and the modified tight-binding approximation (MTBA). The RMTA is based upon the Bloch formulation of the electron-phonon interaction (Bloch, 1928) in which the electron-phonon matrix element  $I_{kk'}^{\alpha} = \langle \psi_k | \hat{x}_{\alpha} \cdot \delta V | \psi_{k'} \rangle$  is calculated using the periodic crystal wave functions  $\psi_k$  and the change in crystal potential due to an atomic displacement  $\delta V$ . The RMTA simply consists in approximating this change  $\delta V$  by

<sup>1</sup>Research sponsored by the Materials Sciences Division, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

By acceptance of this article, the publisher or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering the article.

$\vec{u} \cdot \delta V = \vec{u} \cdot \nabla V$  where  $\vec{u}$  is a small displacement and  $\nabla V$  is the gradient of the crystal potential of the perfect lattice. The name derives from the fact that the crystal potential of transition metals is usually cast into "muffin-tin" form and for a potential of this type the above approximation is equivalent to assuming that when an atom is displaced its muffin-tin potential shifts with it rigidly. One nice feature of the RMTA is that for energy conserving transitions a very simple expression for the matrix elements has been found (Gaspari and Gyorffy, 1972). Given the assumption of a rigid muffin-tin, the remainder of an RMTA calculation for electron-phonon parameters can be performed without further approximation (other than the usual approximations of band theory). We will present evidence that the RMTA is accurate to about 10% for quantities such as the mass enhancement,  $\lambda$ .

The MTBA is based upon the Frölich (Frölich, 1966) formulation of the electron-phonon interaction in which the crystal wave function is expanded in terms of atomic orbitals  $\phi_m(\vec{r}-\vec{R}_i)$  which move with the nucleus as it is displaced. The electron-phonon matrix element is obtained by considering the change in the tight-binding Hamiltonian matrix elements due to an atomic displacement,

$$I_{kk'}^\alpha = \sum_{\substack{ij \\ mn}} [e^{i\vec{k} \cdot \vec{R}_{ij}} - e^{i\vec{k}' \cdot \vec{R}_{ij}}] \hat{x}_\alpha \cdot \nabla_{\vec{R}_{ij}} \langle \phi_m(\vec{r}-\vec{R}_i) | H | \phi_n(\vec{r}-\vec{R}_j) \rangle \quad (1)$$

where  $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$ . A helpful way of remembering the difference between the two approaches is to note that in the Bloch formulation one calculates the *matrix element* of a *potential gradient* while in the Frölich formulation one calculates the *gradient* of the *potential matrix elements*. The MTBA electron-phonon matrix elements are of course never evaluated rigorously using a true tight-binding basis set, although this would be an interesting calculation, instead, the usual procedure is to set up a tight-binding interpolation Hamiltonian with parameters which can be adjusted until agreement is achieved between the tight-binding energy bands and those obtained from a first principles calculation. If additional assumptions are made concerning the dependence of the Hamiltonian matrix elements on intersite separation the electron-phonon matrix elements can be evaluated. There are several variations on the MTBA technique having to do with precisely how one deduces the Hamiltonian matrix elements and their derivatives (Birnboim and Gutfreund, 1975, Peter et al., 1974, and Varma et al., 1979).

Recently, it has been shown that the Bloch and Frölich formulations are equivalent (Ashkenazi et al., 1979, Varma, et al., 1979), and that for energy conserving transitions ( $E_k = E_{k'}$ ) with which we are concerned here it makes no difference whether one calculates the matrix element of the potential gradient or the gradient of the potential matrix element. If the potentials are the same and if both calculations are carried through without further approximation the results should be the same.

## II. RESULTS

Table I displays results of calculations of the Fermi surface average of the square of the electron-phonon matrix element  $\langle I^2 \rangle$ ,

$$\langle I^2 \rangle = \frac{\int \frac{dS_k}{v_k} \int \frac{dS_{k'}}{v_{k'}} \sum_{\alpha} (I_{kk'}^{\alpha})^2}{\left( \int \frac{dS_k}{v_k} \right)^2} . \quad (2)$$

The agreement between the RMTA and empirical values is very gratifying.  $\langle I^2 \rangle$  varies greatly in the transition metals being largest for those materials which show strong d-d inter-site bonding (Nb, Mo, Tc). This variation in  $\langle I^2 \rangle$  when coupled with the known variations in phonon frequencies and in Fermi energy density of states explains the Matthias e/a rules (Matthias, 1957).

TABLE I. Calculated and Empirical Values of  $\langle I^2 \rangle$  for the 4-d Metals

e/a	$\langle I^2 \rangle$			
	Empirical <sup>a</sup>	RMTA <sup>a</sup>	MTBA <sup>b</sup>	MTBA <sup>c</sup>
Y	3	0.0008	0.0021	
Zr	4	0.008	0.007	
Nb	5	0.011	0.0148	0.0144
Mo	6	0.030	0.0235	0.0242
Tc	7	0.024	0.0189	
Ru	8	0.017	0.014	
Rh	9	0.0054 <sup>d</sup>	0.009	
Pd	10	0.0037 <sup>d</sup>	0.0029	

<sup>a</sup>Butler, 1977.

<sup>b</sup>Varma et al., 1979.

<sup>c</sup>Peter et al., 1977.

<sup>d</sup>Estimated from resistivity.

Most MTBA calculations of  $\langle I^2 \rangle$  yield values which are much higher than the empirical ones, but the very recent MTBA results of Varma et al., who use a non-orthogonal basis set and include "p-type" orbitals as well as "s" and "d" are in excellent agreement with the RMTA results. Papaconstantopoulos et al., (1977) have obtained RMTA results very similar to those shown in Table I. Birnboim and Gutfreund, (1975) obtained a value for  $\langle I^2 \rangle$  for Nb of 0.024 using an MTBA approach.

Substantial uncertainty is associated with the empirical estimates of  $\langle I^2 \rangle$  in Table I because they depend on the poorly known values of the Coulomb pseudopotential  $\mu^*$  and upon estimates of the effective mean square phonon frequencies  $\langle \omega^2 \rangle$  defined below. Details of the procedure used in estimating these quantities are given by Butler, (1977). Uncertainties in  $\langle \omega^2 \rangle$  can be avoided by calculating the mass enhancement  $\lambda$  which is defined by

$$\lambda = \frac{\Omega}{(2\pi)^3} \int \frac{dS_k}{v_k} \int \frac{dS_{k'}}{v_{k'}} \sum_{\alpha\beta j} \frac{I_{kk}^\alpha I_{kk'}^\beta \epsilon_j^\alpha(k-k') \epsilon_j^\beta(k-k')}{M\omega_j^2(k-k') \int \frac{dS_k}{v_k}}, \quad (3)$$

and is related to  $\langle I^2 \rangle$  and  $\langle \omega^2 \rangle$  by  $\lambda = N\langle I^2 \rangle / M\langle \omega^2 \rangle$  where  $N$  is the Fermi energy density of states and  $\hat{\epsilon}_j$  is a phonon polarization vector. Table II compares experimental and calculated values of  $\lambda$  for Nb, Mo, and Pd. The RMTA values seem to be about 10% too high for Nb and Pd and essentially exact for Mo (taking  $\mu^*$  to be 0.11).

The uncertainties in  $\mu^*$  can be avoided by calculating the room temperature resistivity which is given by Chakraborty et al., (1976)  $\rho = (3\pi k_B / \hbar e^2 N \langle v^2 \rangle) \lambda_{tr} T$  where  $\langle v^2 \rangle$  is the mean square Fermi velocity and  $\lambda_{tr}$  is a quantity very similar to  $\lambda$

$$\lambda_{tr} = \frac{\Omega}{(2\pi)^3} \int \frac{dS_k}{v_k} \int \frac{dS_{k'}}{v_{k'}} \sum_{\alpha\beta j} \frac{I_{kk}^\alpha I_{kk'}^\beta \epsilon_j^\alpha(k-k') \epsilon_j^\beta(k-k')}{M\omega_j^2(k-k') \int \frac{dS_k}{v_k}} (\vec{v}_k - \vec{v}_{k'})^2. \quad (4)$$

RMTA calculations yield  $\lambda_{tr} = 1.07$  for Nb and  $\lambda_{tr} = 0.46$  for Pd (Pinski et al., 1978a). Both values appear to be about 10% larger than experiment.

TABLE II. Calculated and Empirical Values of  $\lambda$  for Nb, Mo, and Pd

	Empirical <sup>a</sup>	Empirical <sup>b</sup>	Tunneling	RMTA
Nb	0.96	1.04	1.01, <sup>c</sup> 0.98 <sup>d</sup>	1.12 <sup>e</sup>
Mo	0.44			0.40 <sup>f</sup>
Pd		0.38		0.41 <sup>f</sup>

<sup>a</sup>From  $T_c$  using  $\mu^* = 0.13$

<sup>b</sup>From Resistivity:  $\lambda = (\lambda_{tr})_{emp} \times (\lambda/\lambda_{tr})_{calc}$ .

<sup>c</sup>Arnold et al., (1979).|

<sup>d</sup>Robinson and Rowell, (1977).

<sup>e</sup>Butler et al., (1979).

<sup>f</sup>Pinski et al., (1978a).|

More detailed investigations of the strength of the electron-phonon interaction have also been performed. The most detailed information can be obtained from measurements of the phonon linewidth (Allen, 1972). The phonon linewidth  $\gamma_j(q)$  tells the amount of electron-phonon coupling contributed by each particular phonon and is related to  $\lambda$  by

$$\lambda = \sum_{qj} \gamma_j(q) / \pi N \omega_j^2(q) . \quad (5)$$

RMTA calculations (Butler et al., 1977 and Pinski and Butler, 1979a), have successfully predicted two regions of strong electron-phonon coupling before they were observed experimentally (Fig. 1). The peak in the calculated Pd [100] LA linewidth appeared at  $\zeta = 0.34$ , but by identifying the Fermi surface transitions responsible for the peak and using experimental Fermi surface data it was possible to *predict* that the true peak position would be at  $\zeta = 0.4$  in precise agreement with experiment (Youngblood et al., 1979).

Another detailed measure of the electron-phonon interaction is the spectral function  $\alpha^2F(\omega)$  which can be defined as an average over the linewidth

$$\alpha^2F(\omega) = \sum_{qi} \gamma_j(q) \delta[\omega - \omega_j(q)] / 2\pi\omega N . \quad (6)$$

RMTA calculations of  $\alpha^2F(\omega)$  for Nb (Butler et al., 1977, Harmon and Sinha, 1977, and Butler et al., 1979) yield a spectral function which is quite similar in shape to the phonon density

of states (Fig. 2). Similar results have been obtained by the Varma-Weber version of the MTBA (Weber, 1977).

The experimental spectral function of Nb is somewhat controversial. Three experimental spectra are shown in Fig. 2. The differences arise partly from different experimental techniques and partly from different ways of analyzing the tunneling data. The most recent of the experimental spectra (Arnold et al., 1979) shows excellent agreement with the calculation except for the high frequency peak. The phonon linewidth measurements seem to favor the calculated spectrum because they show strong coupling for the longitudinal phonons. It has recently been shown (Otschik, 1978) that any mechanism (e.g., disorder, dissolved oxygen) which decreases the strength of the electron-phonon coupling within  $\approx 50 \text{ \AA}$  of the surface will appear in the deduced spectral function as an enhancement at low frequency and a reduction at high frequency.

Since the shape and strength of the spectral function determine the thermodynamic critical field  $H_c(T/T_c)$ , it is possible in principle to test a proposed spectral function by using it to calculate a deviation function  $D(t) = [H_c(t)/H_c(0)] - (1-t^2)$  which may be compared with experiments. In Fig. 3, we compare the deviation function obtained from the calculated spectral function of Fig. 2 with three sets of experimental data. The agreement is quite good especially with the calorimetric data of Ferreira et al. Unfortunately, the deviation function is insufficiently sensitive to the shape of  $\alpha^2F(\omega)$  and the different sets of experimental data show too much variation to conclusively rule out either the Arnold-Wolf spectrum or the Robinson-Rowell spectrum (Daams and Carbotte, 1978). The deviation function does indicate however that  $\lambda$  is approximately 1.0. It should be noted that the Arnold-Wolf data has  $\lambda$  of about the right magnitude but the deduced  $T_c$  is only 7.9 K and the Robinson-Rowell data although it yields the correct  $T_c$  gives a value for the zero frequency gap which is too low.

The upper critical field  $H_{c2}$  of a cubic type II superconductor is sensitive to anisotropy in the Fermi velocity and in the gap function. Figures 4 and 5 show the results of recent calculations of  $H_{c2}(T, \hat{B})$  for pure Nb. The calculations are based on an extension of the theory of Hohenberg and Werthammer, (1967) and amount to an essentially exact solution of their equations (5) and (26). Fermi velocities were calculated at 1057 points in the irreducible Brillouin zone using Korringa-Kohn-Rostocker band theory and a potential adjusted to give a good fit to Fermi surface data (Butler et al., 1979).

Small strong coupling corrections were applied using the factors  $\eta_{\text{HC}_2}(0)$  and  $\eta_{\text{HC}_2}(1)$  calculated by Rainer and Bergmann, (1974). It is primarily the anisotropy of the Fermi velocity which is responsible for the anisotropy of  $\text{H}_{\text{C}_2}$  and for the deviation of its temperature dependence from that predicted by isotropic theory. The calculated anisotropy in Fig. 4 has the same shape as the experiment but it is somewhat larger. The calculations do not include gap anisotropy because RMTA calculations (Butler et al., 1979 and Pinski and Butler, 1979b) indicate it is ignorably small. MTBA calculations of Peter et al., (1977) yield a larger anisotropy but it is of such character as to increase the observed anisotropy and worsen the agreement with experiment.

#### ACKNOWLEDGMENTS

J. Carbotte, J. M. Daams and B. Mitrovic graciously provided the programs which were used to calculate  $\text{H}_{\text{C}}(\text{T})$ . G. Arnold, E. L. Wolf and R. Kerchner made their data available to us prior to publication. Helpful conversations with P. B. Allen, F. J. Pinski, J. S. Faulkner, J. F. Harris, and G. M. Stocks are gratefully acknowledged. We also extend thanks to G. Gollhofer for rapid and accurate typing of the camera-ready manuscript.

#### REFERENCES

- Allen, P.B. (1972). *Phys. Rev. B* 6, 2577.  
 Arnold, G. B., Zasadzinski, J. Osmun, J. W., and Wolf, E. L. (1979). *Phys. Rev. B* (to be published).  
 Ashkenazi, J., Lacorogna, M., and Peter, M. (1979). *Sol. State Comm.* 29, 181.  
 Birnboim, A. and Gutfreund, H. (1975). *Phys. Rev. B* 12, 2682.  
 Bloch, F. (1928). *Z. Physik* 52, 555.  
 Bostock, J., Lo, K. H., Cheung, W. N., Diadiuk, V., and MacVicar, M.L.A. (1976). In "Superconductivity in d- and f-band Metals," (ed. D. H. Douglass), Plenum, New York.  
 Butler, W. H. (1977). *Phys. Rev. B* 15, 5267.  
 Butler, W. H., Olson, J. J., Faulkner, J. S., and Gyorffy, B. L. (1976). *Phys. Rev. B* 14, 3823.  
 Butler, W. H., Pinski, F. J., and Allen, P. B. (1979). *Phys. Rev. B* 19, 3708.  
 Butler, W. H., Smith, H. G., and Wakabayashi, N. (1977) *Phys. Rev. Lett.* 39, 1004.  
 Chakraborty, B., Pickett, W. E., and Allen, P. B. (1976). *Phys. Rev. B* 14, 3227.  
 Daams, J. M. and Carbotte, J.P. (1978). In "Transition Metals-1977," (eds. M.J.G. Lee, J. M. Perz, E. Fawcett), the Institute of Physics, London.

- Ferreira, J., Burgemeister, E. A., and Dokoupil, A. (1969).  
*Physica* 41, 409.
- Frölich, H. (1966). In "Perspectives in Modern Physics,"  
(R. E. Marshak, ed.) p. 539, Interscience, New York
- Gaspari, G. D. And Gyorffy, B. L. (1972). *Phys. Rev. Lett.* 28,  
801.
- Harmon, B. M. and Sinha, S. K. (1977). *Phys. Rev. B* 16, 3919.
- Hohenberg, P. C. and Werthamer, N. R. (1966). *Phys. Rev.* 153,  
493.
- Kerchner, H. R., Christen, D. K., and SeKula, S. T. (1979).  
*Phys. Rev. B* (to be published) and this volume.
- Leupold, H. A. and Boorse, H. A. (1964). *Phys. Rev.* 134, A1322.
- Matthias, B. T. (1957). In "Progress in Low Temperature  
Physics," (C. J. Gorter, ed.) p. 138, North Holland  
Amsterdam.
- Otschik, P. (1978). *Phys. Stat. Sol. (b)* 88, 563.
- Papaconstantopoulos, D. A., Boyer, L. L., Klein, B. M.,  
Williams, A. R., Moruzzi, V. L., and Janak, J. R. (1977).  
*Phys. Rev. B* 15, 4221.
- Peter, M., Klose, W., Adam, G., and Entel, P. (1974). *Helv.*  
*Phys. Act.* 47, 807.
- Peter, M. Ashkenazi, J., Dacorogna, M. (1977). *Helv. Phys. Act.*  
50, 267.
- Pinski, F. J., Allen, P. B., and Butler, W. H. (1978a). *Phys.*  
*Rev. Lett.* 41, 431.
- Pinski, F. J., Allen, P. B., and Butler, W. H. (1978b). *J.*  
*Phys. (Paris)* 39, C6-233.
- Pinski, F. J. and Butler, W. H. (1979a). *Phys. Rev. B* (in press).
- Pinski, F. J. and Butler, W. H. (1979b). Unpublished.
- Rainer, D. and Bergmann, G. (1974). *J. Low Temp. Phys.* 14, 1974.
- Robinson, B. and Rowell, J. M. (1977). Private communication.
- Shapiro, S. M., Shirane, G., and Axe, J. D. (1975). *Phys. Rev.*  
*B* 12, 4899.
- Varma, C. M., Blount, E. I., Vashishta, P., and Weber, W. (1979).  
*Phys. Rev. B* (in press).
- Weber, W. (1977). Private communication.
- Williamson, S. J. (1970). *Phys. Rev. B* 2, 3545.
- Youngblood, R., Noda, Y., and Shirane, G. (1979). *Phys. Rev. B*  
(in press).

*FIGURE 1(a).* [110] phonon linewidths for Nb. *(b)* [100] phonon linewidths for Pd. Solid (dotted or dashed) histograms are calculated longitudinal (transverse) linewidths. Circles (triangles) with error bars are experimental longitudinal (transverse) linewidths.

*FIGURE 2.* Calculated and experimental spectral functions for Nb. Solid curve is RMTA calculation (Butler et al., 1979), dotted, dashed and chain-dotted curves are experimental results of Arnold et al., (1979), Robinson and Rowell, (1977), and Bostock et al., (1976), respectively.

*FIGURE 3.* Calculated and experimental deviation functions for Nb. Circles, triangles, and +'s are magnetization data (Kerchner et al., 1979) taken with applied field parallel to [100], [110] and [111] directions, respectively. X's and dashed line are calorimetric data of Leupold and Boorse, (1964) and Ferreira et al. (1969), respectively. Solid line is calculated using the RMTA  $\alpha^2F$  of Fig. 2.

*FIGURE 4.* Anisotropy of  $H_{c2}$  for Nb in (110) plane. Solid curve is calculated for  $T = 0$ . Circles are experimental results (Williamson, 1970) for  $T/T_c = 0.04$ .

*Figure 5.* Temperature dependence of  $H_{c2}$  for Nb. Solid curves are calculated results for an applied field in the [111] (upper) [110] (middle) and [100] (lower) directions. Experimental results (Kerchner et al., 1979) are shown by the triangles [111] direction, circles [110] direction, and rectangles [100] direction.









