

SUPERCONDUCTIVITY AND BAND STRUCTURE
FROM A SINGLE PSEUDOPOTENTIAL: ZINC AND CADMIUM

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Three values of the electron-phonon mass enhancement λ for zinc and cadmium are compared: one obtained from the ratio of the electronic-specific-heat density of states and the band-structure value calculated from a pseudopotential approach, one calculated directly by means of the same pseudopotential, and one extracted by other authors from values of the superconducting transition temperature T_c and the Debye temperature Θ . For both metals the agreement between all three λ values is very good, indicating the correctness and uniqueness of the pseudopotential. Calculations performed with other proposed pseudopotentials give very different values of λ .

We want to report in this Letter a remarkable test which we have performed on the validity and uniqueness of the pseudopotential approach. We have calculated by completely different methods two values of the electron-phonon mass enhancement λ and compared these values with each other and with a third empirically determined value. The agreement is very good and therefore gives confidence in the uniqueness of the pseudopotential as well as in the ability of the method to describe accurately such in principle unrelated experiments as the de Haas-van Alphen effect, the electronic specific heat, and the superconducting transition temperature.

Stark and Falicov have proposed¹ an experimentally determined pseudopotential for zinc and cadmium, based on a highly nonlocal model, which they obtained by an overall fitting of the Fermi-surface extremal cross-sectional areas to Stark's own² de Haas-van Alphen frequencies. The band structure obtained agreed with the experimental data to about 1% and had an internal consistency³ which was much better than that. The resulting band structure has been used previously to determine other Fermi-surface parameters⁴ and comparison with experiments has again yielded good agreement. A further comparison with the available optical data⁵ has also resulted in fairly good agreement.⁶ From the above band structure¹ we have calculated the density of

electron states with the results reported in Fig. 1. The density of states at the Fermi level $N_{\text{bs}}(\epsilon_{\text{F}})$, when compared with the same value for the free-electron model $N_{\text{fe}}(\epsilon_{\text{F}}^0)$, yields for the parameter $\rho \equiv N_{\text{bs}}(\epsilon_{\text{F}})/N_{\text{fe}}(\epsilon_{\text{F}}^0)$ the calculated values

$$\rho_1(\text{Zn}) = 0.59, \quad \rho_1(\text{Cd}) = 0.54. \quad (1)$$

From these values the electron-phonon mass enhancement λ can be easily calculated using the experimental values of the coefficient γ of the electronic specific heat^{7,8}:

$$\gamma = \frac{1}{3}\pi^2 k_{\text{B}}^2 N_{\text{bs}}(\epsilon_{\text{F}}) [1 + \lambda]; \quad (2)$$

here k_{B} is the Boltzmann constant. This formula yields

$$\lambda_1(\text{Zn}) = 0.43, \quad \lambda_1(\text{Cd}) = 0.36. \quad (3)$$

We have also calculated λ directly by means of the formula

$$\lambda_2 = N_{\text{bs}}(\epsilon_{\text{F}}) \int \frac{d\Omega_k d\Omega_{k'}}{16\pi^2} \times \sum_{\alpha} |M_{\vec{k}-\vec{k}',\alpha}|^2 \frac{1}{\hbar\omega_{\alpha}(\vec{k}-\vec{k}')}, \quad (4)$$

where \vec{k} and \vec{k}' label electron states at the Fermi surface, α indicates phonon polarization and branch, and the integrations are over solid an-

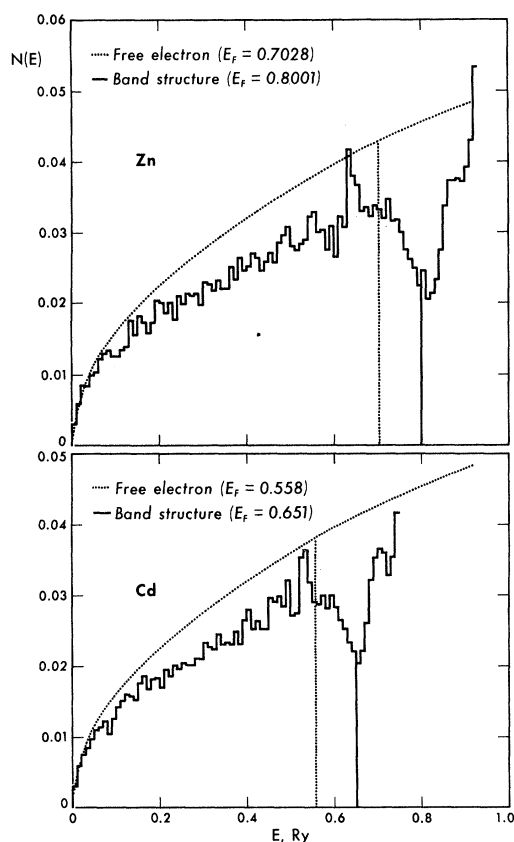


FIG. 1. The density-of-states curves for Zn and Cd. Abscissas are in Rydberg units and ordinates in states/Ry (Bohr radius)³. Corresponding free-electron curves and Fermi energies are also shown.

gles. The electron-phonon matrix element M is given by

$$M_{\vec{k}-\vec{k}+\vec{q}+\vec{G}, \alpha} = -i \left(\frac{\hbar}{2M_0 N \omega_\alpha(\vec{q})} \right)^{1/2} \hat{e}_{\vec{q}\alpha} \cdot (\vec{q} + \vec{G}) \times S(\vec{G}) \langle \vec{k} + \vec{q} + \vec{G} | V | \vec{k} \rangle, \quad (5)$$

where M_0 is the ionic mass, N the number of atoms, $S(\vec{G})$ the structure factor, $\omega_\alpha(\vec{q})$ and $\hat{e}_{\vec{q}\alpha}$ the frequency and polarization of the $\vec{q}\alpha$ phonon, respectively, and \vec{G} is a reciprocal lattice vector which makes \vec{q} lie in the first Brillouin zone. Finally, $\langle \vec{k}' | V | \vec{k} \rangle$ is the matrix element of the pseudopotential between states \vec{k}' and \vec{k} on the Fermi surface.

In order to evaluate (4) and (5) we have represented the six phonon branches by three spherically symmetric modes in an extended zone; one of these branches is taken to be a purely longitudinal mode and the other two are taken to be de-

generate and purely transverse. The extended zone was replaced by an equivalent sphere. The phonon frequencies $\omega_\alpha(\vec{q})$ in zinc were chosen by averaging the values obtained from neutron scattering.⁹ For cadmium, where no neutron data are available, the spectrum was chosen to be identical to that of zinc, but each mode was scaled down by the experimental ratio of sound velocities, as determined from the elastic constants.¹⁰ The matrix element $\langle \vec{k}' | V | \vec{k} \rangle$ was taken to be the nonlocal pseudopotential of Stark and Falicov,¹ with a smooth curve interpolated through the values of $\vec{k}' - \vec{k} = \vec{G}$ (any reciprocal lattice vector) and through the point $-\frac{2}{3}\epsilon_F$ at $\vec{k}' - \vec{k} = 0$; $N_{DS}(\epsilon_F)$ was obtained from (1). The final result was

$$\lambda_2(\text{Zn}) = 0.42, \quad \lambda_2(\text{Cd}) = 0.40, \quad (6)$$

with an estimated accuracy of about 20%.

Several authors^{11,12} have obtained λ from experimental values of the superconducting transition temperature T_C and the Debye temperature Θ . These values involve reasonable assumptions on the value of the Coulomb-interaction parameter μ and the discrepancy between authors is mainly due to different values which μ is assumed to take. McMillan¹¹ obtains

$$\lambda_3(\text{Zn}) = 0.38, \quad \lambda_3(\text{Cd}) = 0.38; \quad (7)$$

while Garland, Bennemann, and Mueller quote

$$\lambda_3(\text{Zn}) = 0.48, \quad \lambda_3(\text{Cd}) = 0.45. \quad (8)$$

Comparison of (3), (6), (7), and (8) shows very good agreement among the four pairs of values, the largest discrepancies appearing between the empirical values (8) of Garland, Bennemann, and Mueller and the other three sets of values. All four pairs are within the uncertainty of the calculation of (6).

One further corroboration of the validity of the pseudopotential proposed by Stark and Falicov comes from the fact that, when the calculation of (4) and (5) was repeated using the Heine-Animalu model potential,¹³ the results were appreciably different:

$$\lambda_2(\text{Zn}) = 0.27, \quad \lambda_2(\text{Cd}) = 0.10; \quad (9)$$

the remarkable agreement was destroyed.

In conclusion we would like to point out that, if the pseudopotential of a given metal were known to be as accurate as we believe the potentials are known in the present case for zinc and cadmium, the path followed by McMillan¹¹ and Garland, Bennemann, and Mueller¹² can be reversed and

the superconducting transition temperature T_c could thus be calculated with a reasonable degree of accuracy. Magnesium,¹⁴ which is known to be normal to temperatures down to about 20 mdeg,¹⁵ could be a good test case.

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¹R. W. Stark and L. M. Falicov, Phys. Rev. Letters **19**, 795 (1967), and to be published.

²R. W. Stark, to be published.

³The number of electrons in the Fermi distribution was accurate to about 1 part in 2000.

⁴R. C. Jones, R. G. Goodrich, and L. M. Falicov, Phys. Rev. **174**, 672 (1968).

⁵A. H. Lettington in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland Publishing Company, Amsterdam, The Netherlands, 1966), p. 147; R. H. W. Graves and A. P.

Lenham, J. Opt. Soc. Am. **58**, 126 (1968).

⁶R. V. Kasowski, to be published.

⁷G. Seidel and P. H. Keesom, Phys. Rev. **112**, 1083 (1958).

⁸N. E. Phillips, Phys. Rev. **134**, A385 (1964).

⁹G. Borgonovi, G. Caglioti, and J. J. Antal, Phys. Rev. **132**, 683 (1963); E. Maliszewski, J. Rosolowski, D. Sledziewska, and A. Czachor, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, London, 1965), p. 33.

¹⁰G. A. Alers and J. R. Neighbors, J. Phys. Chem. Solids **7**, 58 (1958); C. W. Garland and J. Silverman, Phys. Rev. **119**, 1218 (1960), and **127**, 2287 (1962).

¹¹W. L. McMillan, Phys. Rev. **167**, 331 (1968).

¹²J. W. Garland, K. H. Bennemann, and F. M. Mueller, Phys. Rev. Letters **21**, 1315 (1968).

¹³A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).

¹⁴J. C. Kimball, R. W. Stark, and F. M. Mueller, Phys. Rev. **162**, 600 (1967).

¹⁵N. Kurti and F. Simon, Proc. Roy. Soc. (London), Ser. A **151**, 610 (1935); R. L. Falge, Jr., N. M. Wolcott, R. A. Hein, J. E. Cox, and J. W. Gibson, Bull. Am. Phys. Soc. **13**, 730 (1968).

THEORY OF INDIRECT NUCLEAR-SPIN INTERACTIONS IN LEAD*

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The Ruderman-Kittel (A_{12}) and pseudodipolar coupling constants (B_{12}) in lead have been calculated relativistically using a procedure developed earlier and adapted to Dirac orthogonalized-plane-wave functions. For the conduction electrons, pseudo wave functions were obtained from the pseudopotential parameters of Anderson and Gold, the plane waves in the linear combination being replaced by Dirac orthogonalized-plane-wave functions. Our theoretical values for A_{12} and B_{12} are 4811 and 1477 cps, respectively, in reasonable agreement with experimental values of 4800 ± 500 and 2200 ± 200 cps.

The indirect spin-spin interactions^{1,2} characterized by the Ruderman-Kittel (RK) and pseudodipolar (PD) parameters A_{12} and B_{12} , respectively, in metallic lead, have recently been studied by Alloul and Froidevaux³ using the spin-echo technique.⁴ In trying to obtain a theoretical estimate of A_{12} to compare with their experimental result, these authors utilized the RK approximation which replaces the k -dependent spin densities and effective masses involved in the theory by their values at the Fermi surface. Using the free-electron Fermi momentum, these authors obtained a vanishingly small theoretical value for A_{12} as compared with 4800 ± 500 cps from experiment.³ Evidently, a more detailed analysis involving the \vec{k} dependence of the pertinent quantities involved in the theory,⁵ together with a proper consideration of the relativistic nature of this

heavy metal, is required. Such a theory has recently been developed⁶ in terms of Dirac orthogonalized-plane-wave (DOPW) functions and applied to the alkali metals rubidium and cesium. It is particularly interesting to apply this theory to a heavy metal like lead where relativistic effects are of much greater importance as compared with the alkali metals. A second motivation for the present application to lead is that for the alkali metals, the disturbing result was obtained that the theoretical values of B_{12} were an order of magnitude smaller than experiment. Since the experimental values of B_{12} in the alkali metals were rather small, it was not clear whether the origin of the discrepancy was to be ascribed to a weakness of the theory or inaccuracy of experimental results. A more definitive answer on this point is expected from calculations on lead