

TABLE I. Tabulated data for the superconductors.*

Element	T_c (°K)	V (cc)	$(\gamma \times 10^4)**$	$(\gamma \times 10^4)***$	Θ (°K)
"Soft" Superconductors					
Pb	7.22	18.2	7.1 ^{a, b}	—	90 ⁱ
Hg	4.15	13.4	3.75 ^a —4.5 ^c	—	96 ⁱ
Sn	3.71	16.2	3.45 ^a —3.95 ^b	4.0 ^d	185—260 ⁱ
In	3.38	15.8	3.5 ^b —3.6 ^e	—	110
Tl	2.4	17.3	2.8 ^b —3.4 ^c	—	90—100 ⁱ
Al	1.15	10.1	2.59 ^e	3.48 ^f	390—420 ⁱ
Ga	1.12	11.75	0.8 ^g —1.5 ^g	—	240
Zn	0.95	9.15	1.36 ^e	1.25 ^h —1.5 ⁱ	290—320 ⁱ
Cd	0.54	13.0	0.75 ^g	—	170 ^j
"Hard" Superconductors					
Th	1.3	20.5	7.1 ^k	—	170 ^j
Ta	4.4	10.9	14.1 ^l	—	240 ^j

* T_c is the transition temperature, V is the atomic volume, γ is the normal electronic specific heat coefficient, and Θ is the Debye temperature.

** γ is given in units of cal./mole-deg.². The values in this column for the soft superconductors are obtained from magnetic measurements of the threshold curves.

*** γ is given in units of cal./mole-deg.². The values in this column for the soft superconductors are obtained from calorimetric measurements.

^a J. G. Daunt and K. Mendelsohn, Proc. Roy. Soc. A160, 127 (1937).

^b Daunt, Horseman, and Mendelsohn, Phil. Mag. 27, 754 (1937).

^c A. D. Misener, Proc. Roy. Soc. A174, 262 (1940).

^d W. H. Keesom and P. H. Van Laer, Physica 5, 193 (1938).

^e J. G. Daunt and C. V. Heer, Phys. Rev. 76, 1324 (1949).

^f J. A. Kok and W. H. Keesom, Physica 4, 835 (1937).

^g Results to be reported subsequently.

^h W. H. Keesom and J. N. van den Ende, Proc. Amst. Akad. Sci. 35, 143 (1932).

ⁱ A. A. Silvidi and J. G. Daunt, Phys. Rev. 77, 125 (1950).

^j Burton, Grayson-Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York, 1940), p. 347.

^k Calculated from Eq. (2) using Schoenberg's data, reference 7.

^l From calorimetric data of Keesom and Desirant, reference 8.

paid to the problem of superconductivity it is thought worth while to point out one empirical correlation which concerns the electronic structure.

Recent measurements⁶ of the magnetic properties of pure Ga and Cd in the superconducting state below 1°K have completed all the data necessary for the calculation of the electronic specific heat of the normal state ($C_{el} = \gamma T$) for all the known "soft" superconductors. In Table I, the Sommerfeld γ -values have been tabulated together with other pertinent data for the superconductors. It is to be noticed that the γ -values increase approximately linearly with increasing transition temperature, T_c , such that

$$\gamma = AT_c \quad (1)$$

where $A \approx 1 \times 10^{-4}$ cal./mole-degree². Al, however, appears to be exceptional, but in view of its high Debye temperature as compared with the other soft superconductors, it may not be strictly permissible to class it in the same grouping.

No similar complete data can be tabulated for the hard superconductors since with the possible exceptions of thorium measured magnetically by Schoenberg⁷ and of Ta measured calorimetrically by Keesom and Desirant,⁸ either their observed magnetic threshold curves do not represent a reversible equilibrium boundary between the normal and superconductive states thus allowing no reliable derivation of γ or no calorimetric observations at low temperatures have been made. The pertinent data for Th and Ta are included in Table I, the γ -value for Th being calculated from Schoenberg's data⁷ using the equation that can be derived for γ from Gorter and Casimir's thermodynamical theory⁹ assuming a parabolic magnetic threshold curve, namely

$$\gamma = (V/8\pi)(dH_c/dT)^2 T = T_c. \quad (2)$$

From Table I it can be deduced that if the γ -values of Ta and Th satisfied an equation of type (1), it would be with a value of the constant A more than three times larger than that for the soft superconductors. More data here would be of value; for example, calorimetric measurements of γ for such readily obtainable metals as Nb, V, and Ti would be of interest.

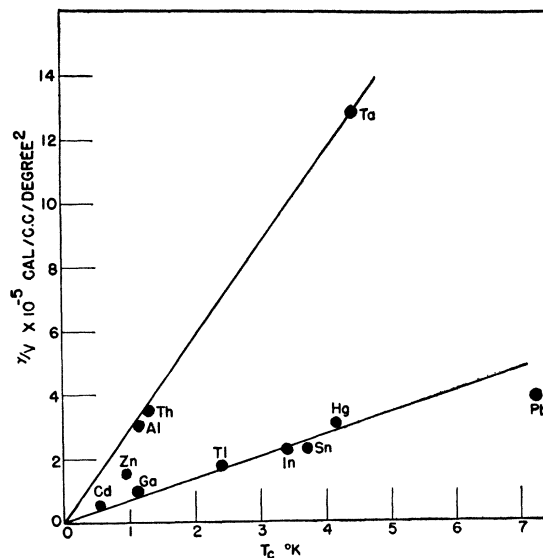


FIG. 1. Variation of γ/V with T_c , showing the division into "hard" and "soft" superconductors.

As a first approximation it would be expected that the interaction energy between the electrons responsible for the condensation into the superconductive state would increase with increasing number density of electrons and hence on the Sommerfeld theory¹⁰ with the quotient γ/V where V is the atomic volume. It seemed to be of interest, therefore, to examine the empirical relationship between kT_c and γ/V . A plot of the experimentally observed values of γ/V against T_c is given in Fig. 1, for the elements listed in Table I, the γ -values being taken as the mean of those listed in the above tables. It will be seen that with exception of Zn the elements fall along two approximately straight lines, one for the soft superconductors and another for the hard superconductors (which group appears to include Al). The difference between the groups is not surprising in view of the known differences in their electronic band structures.

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- ² Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. 78, 487 (1950).
- ³ G. J. Sizoo and H. K. Onnes, Leiden Communications, Nos. 133 and 180b; N. Alekseyevsky, J. Phys. U.S.S.R. 9, 147 (1945); B. Lasarew and A. Galkin, J. Phys. U.S.S.R. 8, 376 (1944).
- ⁴ J. Bardeen, Phys. Rev. 79, 167 (1950).
- ⁵ H. Froehlich, Phys. Rev. 79, 845 (1950).
- ⁶ J. G. Daunt, to be reported later.
- ⁷ D. Schoenberg, Proc. Camb. Phil. Soc. 36, 84 (1940).
- ⁸ W. H. Keesom and M. C. Desirant, Physica 8, 273 (1941).
- ⁹ C. J. Gorter and H. G. B. Casimir, Physica 1, 305 (1934).
- ¹⁰ A. Sommerfeld, Zeits. f. Physik 47, 1 (1928).

On the Cohesive Energy of Metallic Lithium

R. A. SILVERMAN AND W. KOHN*
Harvard University, Cambridge, Massachusetts
October 13, 1950

ON the basis of the Wigner-Seitz atomic sphere approximation, Bardeen¹ has evaluated the first two terms of a series expansion for the energy $E(k)$ of an electron with wave number k moving in the lattice of metallic Li. He found that $E(k) = E_0 + E_2 k^2 + E_4 k^4 + \dots$, where $E_0 = -0.6635$ and $E_2 = 0.6539$ for the experimentally determined lattice constant² of 3.4492 Å. Bardeen's calculations were based on the Li ion-core potential published by

TABLE I. Cohesive energy of metallic lithium by various methods of calculation.

Method used	Cohesive energy (kcal./mole)
Experimental	39.0
Power series to order k^2	35.2
Variable coefficients using (4)	34.6
Power series to order k^4	34.9
Variable coefficients using (5)	34.8

Seitz⁴ which, as a result of an error, differed somewhat from the potential which Seitz had actually used. Bardeen has forwarded to us the correct potential and with it we have repeated his calculation with the results $E_0 = -0.6832$, $E_2 = 0.7270$. These values differ only slightly from those calculated by Seitz⁴ who used a perturbation method (-0.682 and 0.744). With our values of E_0 and E_2 and the expression $(0.284/r_s) - [0.58/(r_s + 5.1)]$ ($r_s =$ radius of Wigner-Seitz sphere) usually assumed as the correction resulting from correlations between electrons, one finds the value of 35.2 kcal./mole for the cohesive energy of metallic Li, as compared with the experimental value⁵ of 39.0 kcal./mole. (The theoretical values of Seitz and Bardeen were 33.7 and 33.9 kcal./mole respectively.)

On the basis of order of magnitude estimates it was thought that a considerable part of the discrepancy between theory and experiment might be due to the fourth-order term in the series expansion of $E(k)$. We therefore evaluated E_4 by an extension of Bardeen's method. This required the calculation of the lattice wave function to order k^2 .

$$\psi_k = [u_0 + ikP_1\phi_1 + k^2(\phi_0 + P_2\phi_2)] \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (1)$$

where u_0 is the normalized s -solution of the Schroedinger equation for energy E_0 , ϕ_1 is rv of Bardeen's paper,¹ P_1 and P_2 are the Legendre polynomials of degree 1 and 2 respectively, while ϕ_0 and ϕ_2 are given by the following expressions:⁶

$$\phi_0 = \frac{1}{3}r^2v_1 - \frac{1}{3}r^2u_0 + E_2(du_0/dE)E = E_0 \quad (2)$$

$$\phi_2 = \frac{1}{3}r^2v_1 - \frac{1}{3}r^2u_0 + c_D f_D. \quad (3)$$

Here rv_1 is the radial part of the p -solution as defined by Bardeen and f_D the radial part of the d -solution (again for energy E_0); c_D is chosen in such a way that ϕ_2 satisfies the boundary condition $\phi_2'(r_s) = 0$.

By expanding in power series the expectation value of the Hamiltonian computed with the function (1), one obtains the energy $E(k)$ correct to order k^4 . In this way we found $E_4 = 0.0175$, an unexpectedly small value which does not appreciably change the second-order result for the cohesive energy. (Table I.)

To extract the optimum result from our wave functions we have also computed $E(k)$ using the modified functions

$$\psi_k^{(1)} = [c_1u_0 + ic_2P_1\phi_1] \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (4)$$

and

$$\psi_k^{(2)} = [c_1u_0 + ic_2P_1\phi_1 + c_3(\phi_0 + P_2\phi_2)] \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (5)$$

and adjusting the coefficients c_i to make the expectation value of the Hamiltonian an extremum. Table I summarizes our results.

One notes that none of these refinements of Bardeen's work appreciably improves the agreement with experiment.

It should be mentioned in this connection that the atomic sphere approximation on which the above calculations were based cannot be expected to be reliable near the top of an energy band. One of us (W. Kohn) is therefore investigating the cohesive energy by means of a variation iteration procedure based on the integral equation

$$\psi_k(\mathbf{r}) = \int G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi_k(\mathbf{r}') d\mathbf{r}',$$

where G is the Green's function appropriate to a periodic lattice

and V is the lattice potential. This method takes into account the actual shape of the atomic polyhedron and should give a better description of the upper part of the energy band.

* Now at Carnegie Institute of Technology, Pittsburgh, Pennsylvania.
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² Atomic units are used throughout.
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⁵ Bichowsky and Rossini, *Thermochemistry of Chemical Substances*, (Rheinhold Publishing Corporation, New York, 1936).
⁶ Equations (1) and (2) agree with the expressions derived in Appendix III of Herring and Hill, Phys. Rev. **58**, 132 (1940).

Remarks on the Nuclear Resonance Shift in Metallic Lithium

W. KOHN

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

N. BLOEMBERGEN*

Harvard University, Cambridge, Massachusetts

October 13, 1950

RECENTLY Knight¹ has found that the nuclear resonance frequency for an atom in the metallic state exceeds the frequency of the same atom in a non-metallic compound in the same external field. Townes, Herring, and Knight² have subsequently proposed a simple theory for this effect. They find that for lithium the fractional frequency shift (for a given external magnetic field) is given by

$$\Delta f/f = 155\chi_p \cdot P_F/P_A; \quad (1)$$

here χ_p is the spin contribution to the paramagnetic susceptibility of metallic lithium per unit mass, and $P_F = |\psi_F(0)|^2_{Av}$, $P_A = |\psi_A(0)|^2$ are the mean probability densities at the nucleus of an electron on the Fermi surface of metallic lithium and of the S -electron in the lithium atom respectively.

Using the experimental results¹ $\Delta f/f = 3.6 \times 10^{-4}$ and^{2,3} $\chi_p = 3.0 \times 10^{-6}$ one is led to the experimental value,

$$P_F/P_A = 0.77 \quad (2)$$

for the ratio occurring in (1). Townes *et al.*² estimated on theoretical grounds that this ratio had a value near 0.8, but they did not actually calculate P_F since the then available wave functions were based on an incorrect ion potential.

The correct ion-core potential, calculated by Seitz, has been kindly supplied to us by Bardeen. For atomic lithium it gives $P_A = 0.22$. This value is also checked within a few percent by the measured hyperfine structure separation of the ground state of lithium.⁴

For metallic lithium we have used the wave function (5) of the preceding letter⁵ which was calculated by means of an extension of the Wigner-Seitz-Bardeen theory. It gives $P_F = 0.30$.

Thus, according to theory,

$$P_F/P_A = 1.4. \quad (3)$$

The agreement between theory and experiment is seen to be much worse than was anticipated by Townes *et al.* If one assumes that the difficult measurement of χ_p , which enters into (2), can be relied on, the large discrepancy between theory and experiment is probably due to the theoretical value of P_F . This would indicate that the Wigner-Seitz-Bardeen method is not suitable for a description of the electrons on the Fermi surface of metallic lithium.⁵

* Society of Fellows.

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