

Superconductivity and Mixed Conduction

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The BCS-formula for the energy gap ΔE is extended to include the magnetic exchange interaction of electrons with holes. With the improved expression for ΔE the transition temperatures of Al₅-structures are computed and found to be in a satisfactory agreement with the experimental values.

The discoveries of superconductivity (Kamerlingh-Onnes, 1911) and the Meißner-Ochsenfeld-Effect (1933) were followed by phenomenological theories [1–3], which have been successful in explaining macroscopic magnetic field distributions in superconductors and thermodynamic relationships.

The assumption of an energy gap ΔE at the Fermi level, which at zero temperature separates the occupied deeper lying states from the continuum of unoccupied states, was a first step towards a microscopic theory of superconductivity [4]. For the explanation of this gap various propositions have been made. In 1948 the author proposed the magnetic exchange interaction between electrons and holes to be responsible for the existence of a gap [5] and tried to explain on this basis the appearance of superconductivity in the periodic table [6]. The best known theory for the explanation of a gap is, however, the BCS-theory [7], in which the deep lying energy state is assumed to be produced by a pairing of two s-electrons (Cooper pairs) coupled by lattice oscillations. The electrical zero-point current and the mechanical zero-point momentum of a Cooper pair are zero, its charge is twice that of an electron. Cooper pairs are regarded as the carriers of the current in superconductors. At temperature $T > T_c$, $kT_c \approx \Delta E$, the pairs are broken up and superconductivity disappears.

Theories based on the assumption of an energy gap have met with great success, particularly in explaining characteristic properties of superconductors such as the exponential disappearance of the electronic specific heat and the phase transition between the superconducting and the normal conducting state in a magnetic field, cf. e. g. [8, 9]. There are, however, other important questions which these theories

have as yet not been able to answer in a satisfactory way, for example that of infinite conductivity and the occurrence of superconductivity in elements and compounds, nor can the critical temperatures be correctly predicted, cf. e. g. [10–12]. For these reasons the author has modified and extended the BCS formula for ΔE to include the magnetic exchange interaction term ΔE_{magn} and a subtractive Coulomb interaction term $\Delta E_{\text{coul red}}$. Presently an explicit expression for each of the three terms can be given:

$$\begin{aligned}\Delta E &= -\Delta E_{\text{coul red}} + \Delta E_{\text{latt vibr}} + \Delta E_{\text{magn}} \\ &= e^2 \left[-\left(\frac{6(n-p)^2}{\pi \bar{n}} \right)^{1/3} + \frac{6}{\pi} \bar{n} \left(\frac{\hbar^2}{KM} \right)^{1/2} + 6\pi \bar{n} \frac{\hbar^2}{m^2 c^2} \right];\end{aligned}$$

n, p electron and hole densities, respectively, in the normal conducting state;

$\bar{n} = \bar{p}$ electron (or hole) density in the superconducting state = average of n and p ;

K force constant;

M atomic mass;

m electronic mass;

\hbar Planck constant/2 π ;

c speed of light.

The occurrence of n and p in the equation indicates that doubly charged Cooper pairs have been replaced by neutral electron-hole pairs. The new pair concept allows also to modify the original BCS expression for $\Delta E_{\text{latt vibr}}$. The interaction of the electron-hole pairs with the lattice waves, as presently expressed in a crude approximation of the complex behaviour of lattice vibrations by the zero-point energy $\frac{1}{2} \hbar \omega$ or one force constant and the atomic mass, can be calculated in a classical physical way. This method avoids the typical BCS-factor $\exp(-1/NV)$ with its inherent parameters λ and μ^* , which are difficult to calculate. This does not mean that the BCS-theory is incorrect. The idea of

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electron-hole pairs signifies only a different approach to the problem tackled in the BCS-theory by Cooper pairs.

The formula for ΔE allows a comprehensive survey of the transition temperatures in the periodic system to be made for small values of n, p . In these cases we have $\Delta E_{\text{coul red}} \approx \Delta E_{\text{magn}}$. The magnitude of ΔE is determined by $\Delta E_{\text{latt vibr}}$, which includes the isotope effect.

For high values of n, p and K, M , realised in the A 15-structures, ΔE_{magn} is greater than $\Delta E_{\text{latt vibr}}$ and $\Delta E_{\text{coul red}}$. In this case it is particularly easy to estimate the transition temperatures which, for the most part, can be attributed to the magnetic exchange interaction and show almost no isotope effect [13]. The physical meaning of the magnetic interaction is $\Delta E_{\text{magn}} = 2(e^2/\delta)(v/c)^2$, where $\delta = (6\bar{n}/\pi)^{-1/3}$ and v is the maximum translatory zero-point velocity of electrons or holes, respectively. The required information about this velocity can be easily obtained by a pseudo-potential method in its simplest form, which is mathematically analogous to the old theory of the dielectric constant as derived by Clausius and Mosotti [14]. With this method, a satisfactory agreement between theoretical [15] and experimental [16, 17] values of the critical temperature of A 15 compounds [18, 19] can be obtained, as is shown in Table 1.

Table 1. Transition Temperatures T_c/K of A 15 Structures.

	I	II	III
V_3Al	↓ 11.65	↓ 17.94	↓ 14.8
V_3Ga	16.5	19.0	23.0
V_3In	↑ 13.9	↑ 14.4	
V_3Tl	< 4.2		
V_3Si	↑ 17.1	20.7	↑ 18.4
V_3Ge	6.01		5.3
V_3Sn	3.80		1.9
V_3Pb	< 4.2		
Nb_3Al	↓ 18.80	↓ 22.1	↑ 25.1
Nb_3Ga	20.3	22.8	22.5
Nb_3In	↑ 9.2	↑ 17.8	
Nb_3Tl			
Nb_3Si	↑ > 19.0	↑ 29.3	3.4
Nb_3Ge	23.2	26.4	8.2
Nb_3Sn	18.0	19.9	↓ 12.6
Nb_3Pb	< 1.20		

I Experimental values [16, 17], the highest values have been taken.

II Values calculated by the author from ΔE_{magn} [15].

III Calculated values according to B. M. Klein, L. L. Boyer, and D. A. Papaconstantopoulos [20].

The arrows indicate increasing T_c .

The author considers the intra band symmetry, a special property of the "tight binding approximation" of the electron theory of metals [21, 22], as the cause of an electrically neutral pairing of an electron (charge $-e$) with a defect electron or hole (charge $+e$) coupled by long wavelength lattice oscillations and magnetic exchange interactions. This approximation states that the inversion surface (given by the "Freiheitszahl" $f=0$ or the effective masses $m_{\text{eff}} = \pm \infty$) divides the valence band into two halves which contain the same number of states. For each point on the inversion surface a one to one mapping can be made; the zero-point of the Brillouin zone is mapped to the eight corners. As a result, at the corresponding points the energy (with respect to $f=0$) and the state mass are antisymmetrised, while the translatory velocity and electronic charge ($-e$) are symmetrical properties. If the part above $f=0$ is described by hole eigenfunctions, the antisymmetry of the masses becomes an antisymmetry of the charges and the symmetry of charges a symmetry of the masses.

Up to now the multi-valent metals have been described by the overlapping of two or more energy bands; in the terminology presented here, this becomes an overlapping of an electron- and a hole-band. The concept of a pairing of an electron with a hole would prevent superconduction in pure electron conductors (Alkali metals, Cu, Ag). Only mixed conductors [6, 15], in which the electric current is carried by electrons and holes (in some cases only just prior to the onset of superconductivity), could become superconductors; this is borne out by experimental results. The achievement of exact symmetry required between electrons and holes is made possible by lattice changes which have long been observed in A 15 structures e.g. the transition from cubic to tetrahedral in V_3Si and Nb_3Ge [23].

The wave function of an electron-hole pair is given initially by the determinant of the wave function of the occupied electron states in which the wave function of one hole (at the Fermi energy) is included. If this wave function is used to calculate the magnetic exchange interaction of the hole with all the electrons of equal spin, it can be seen that the interaction behaves as if a single electron with charge ($-e$) were localized at a distance δ around the hole. It is proposed to use the name delta-electron or deltatron for the new quasi-particle. More precisely we should also speak of defect-

electron — delta-electron pairs (or the reverse) or, more concisely, hole-electron pairs (or the reverse).

The momentum of an electron-hole pair is zero, its electrical current is, however, twice the zero-point current of a single electron. Electron-hole pairs, in so far as they can be attributed to lattice interactions, and Cooper pairs exhibit the isotope effect [24]. For the Doll-Naebauer effect [25, 26] the doubled current appears in place of the doubled

charge. Due to the double charge, the Cooper pairs as a unit will be scattered four times more strongly than a single electron — the electrical resistance should be raised by a factor four — whereas with neutral electron-hole pairs scattering processes become insignificant and true superconduction is possible.

In a subsequent paper detailed information about the improved theory will be given.

- [1] R. Becker, F. Sauter, and G. Heller, *Z. Physik* **85**, 772 (1933).
- [2] C. J. Gorter and H. B. G. Casimir, *Physica* **1**, 306 (1934).
- [3] F. London and H. London, *Proc. Roy. Soc. London A* **149**, 72 (1935).
- [4] H. Welker, *Z. techn. Phys.* **19**, 606 (1938).
- [5] H. Welker, *Z. Naturforsch.* **3a**, 461 (1948).
- [6] H. Welker, *Ann. Phys.* **5**, 1 (1949).
- [7] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
- [8] H. Welker, *Physik. Z.* **44**, 134 (1943), cf. p. 138.
- [9] J. R. Schrieffer, *Theory of Superconductivity*, W. A. Benjamin, New York 1964, cf. p. 54.
- [10] M. Peter, J. Ashkenazi, and M. Dacorogna, *Helv. Physica Acta* **51**, 775 (1978).
- [11] B. M. Klein, L. L. Boyer, D. A. Papaconstantopoulos, and L. F. Mattheis, *Phys. Rev. B* **18**, 6411 (1978), cf. p. 6428.
- [12] D. Glötzel, D. Rainer, and H. R. Schober, *Z. Physik B* **35**, 317 (1979).
- [13] J. J. Engelhardt, G. W. Webb, and B. T. Matthias, *Science* **155**, 191 (1967).
- [14] R. Becker and F. Sauter, *Theorie der Elektrizität*, Vol. III, Teubner 1968, cf. p. 127—131.
- [15] H. Welker, *S.-B. math. naturwiss. Abt. Bayer. Akad. Wiss.* **37** (1980), cf. p. 46/47.
- [16] Yu. A. Izyumov and Z. Z. Kurmaev, *Sov. Phys.-Usp.* **17**, 356 (1974), Table I.
- [17] J. Muller, *Rep. Prog. Phys.* **43**, 641 (1980), Table 2.
- [18] G. F. Hardy and J. D. Hulm, *Phys. Rev.* **87**, 884 (1953).
- [19] B. T. Matthias, T. H. Geballe, and V. B. Compton, *Rev. Mod. Phys.* **35**, 1 (1963).
- [20] B. M. Klein, L. L. Boyer, and D. A. Papaconstantopoulos, *Phys. Rev. Lett.* **42**, 530 (1979), cf. p. 531, Table 1.
- [21] H. Fröhlich, *Elektronentheorie der Metalle*, Julius Springer, Berlin 1936, cf. p. 30—38.
- [22] A. Sommerfeld and H. Bethe, *Elektronentheorie der Metalle*, *Handb. d. Phys.* XXIV/2, Julius Springer, Berlin 1933, cf. p. 394—407.
- [23] L. R. Testardi and T. B. Batemann, *Phys. Rev.* **154**, 402 (1967).
- [24] W. Buckel, *Supraleitung*, Physik Verlag, Weinheim 1972, cf. p. 43—45.
- [25] R. Doll and M. Nähbauer, *Phys. Rev. Lett.* **7**, 51 (1961).
- [26] B. S. Deaver and W. M. Fairbank, *Phys. Rev. Lett.* **7**, 43 (1961).