

CHAPTER IV
ISOTOPE EFFECT IN SUPERCONDUCTORS

Introduction

Apart from the basic phenomena, the zero resistance and the Meissner effect in the superconducting state, there is an important property of all superconductors which concerns the dependence of critical temperature, T_c on the average isotopic mass. This investigation was first made by E. Maxwell [71] in Hg^{199} and Hg^{202} (The isotoped metal had been enriched by electromagnetic separation and was purified by triple distillation, the neutral metal was purified by double distillation.), and by Reynolds, Serin and Nesbitt [72] in isotoped mercury with average masses 203.4, 202.0, 200.7, and 199.7 respectively. They also had undertaken similar investigations with the lighter isotopes, having higher transition temperatures.

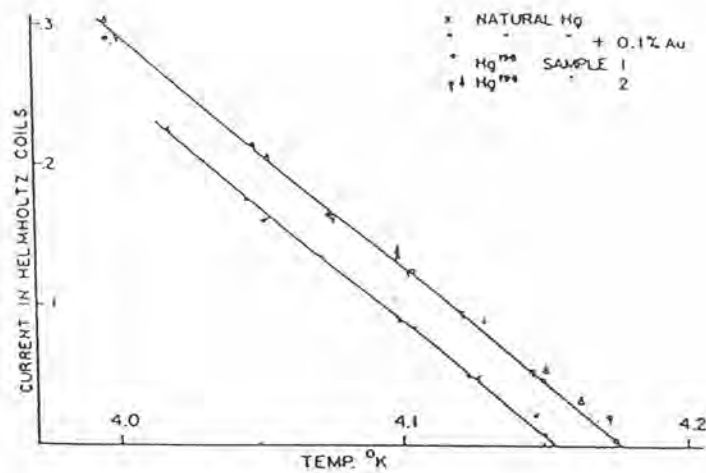


Fig. 13 Current in the Helmholtz coils at the critical field vs. the absolute temperature.

Table 3. Transition temperatures for mercury isotops

Sample	Average mass number	T_c (K)
1	203.4	4.126
2	202.0	4.143
3	200.7	4.150
4	199.7	4.161

This systematic decrease of the transition temperature with increasing mass is called the isotope effect, in Fig. 13, E. Maxwell plotted the current in the Helmholtz coils at the critical field with the absolute temperature for both natural Hg^{200.6} and the isotope Hg¹⁹⁸. The intercepts are significant and give the transition temperature as 4.156 K for natural Hg and 4.177 K for Hg¹⁹⁸, and in Table 3, the critical temperatures for the mercury isotopes are taken as those obtained by Reynolds, Serin and Nesbitt [73].

Further, Reynolds Serin, and Nesbitt [73] tried to find the functional relationship for the isotope effect and showed that the product $M^{1/2}T_c$ is quite constant and is constant than any other simple combination of this variables. The constancy of this product can be interpreted as showing that the ratio of the transition temperature to the Debye temperature of each of the lattices of the different isotope is constant. In the other experiments, with Pb and Sn [74-76], an indication is also given by the product $M^{1/2}T_c$. These results lend support to the theories developed by Fröhlich[77] and Bardeen[78] which take the view that the superconductivity is caused fundamentally by an interaction between the electron in the metal and the variational field of the crystal lattice.

Isotope Effect and Lattice Properties in Superconductivity [79]

In the previous section, it should be pointed out that the data represents a relatively small spread in M and T_c and consequently, in trying to fit a relation of the form $M^\alpha T_c = \text{constant}$, one finds that the product is approximately constant, to the degree noted by Reynolds, Serin, and Nesbitt [73] for a comparatively large range of α 's. Examination of the available data on the isotopes of mercury for the purpose of determining the best value for the exponent. This data is given in Table 4 and is plotted for mercury in logarithmic form in Fig. 14.

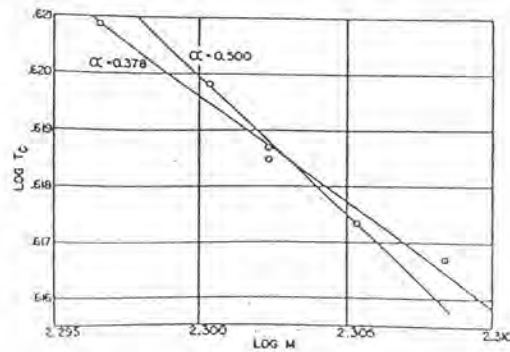


Fig. 14 Plot of $\log T_c$ vs. $\log M$ for mercury

Table 4 Isotope massed and the transition temperature for Hg and Sn.

Element	Mass	T_c (K)
Hg ¹⁹⁸	198.0	4.177
Hg ¹⁹⁹	199.7	4.167
Nat. Hg	200.6	4.154
Nat. Hg	200.6	4.156
Hg ²⁰²	202.0	4.147
Hg ²⁰⁴	203.4	4.137
Sn ¹²⁴	123.1	3.66
Nat. Sn	118.7	3.71

A least-squares fit of the best straight line to the points in Fig. 14 yields a slope of 0.378 ± 0.021 , a line of slope 1/2 is shown for purposes of comparison. The isotope effect of Sn^{124} tends to reinforce this conclusion. One finds a value of 0.394 for the exponent using the data for tin.

We may ask whether the equation, $M^{0.378}T_c = \text{constant}$, corresponds to the invariant of any significant physical quantity. In Table 5 is a listing of the relation between M and T_c which would hold if various quantities have critical values (independent of the particular isotope) at the transition temperature. From a purely empirical point of view the total thermal energy of the lattice is indicated as a first choice and the ideal part of the normal conductivity as a second. This suggestion lends to the ideal that the fundamental interaction of superconductivity is essentially given by the BCS theory as we see in the chapter two.

Table 5. Possible theoretical relations of the form $M^\alpha T_c = \text{constant}$.

Physical quantity (assume constant)	Relation between M and T_c
Thermal energy of the lattice	$M^{3/8}T_c = \text{constant}^a$
Ratio of the thermal energy at the zero-point energy	$M^{1/2}T_c = \text{constant}^a$
Mean square linear momentum	$M^{5/8}T_c = \text{constant}^a$
Mean square thermal velocity	$M^{1/8}T_c = \text{constant}^a$
Ideal part of normal conductivity just before transition	$M^{2/5}T_c = \text{constant}^b$

a From the Debye theory.

b A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Springer, Berlin 1933) Vol.24, part 2, p. 529, Eq. (37.16).

BCS Theory and Isotope Effect

The essence of the BCS theory [43], the microscopic theory of the classical superconductor, is that the electron-phonon interaction plays a key role in producing superconductivity. According to this theory, this mechanism leads to an attractive interaction between electrons within a characteristic phonon energy $\hbar\omega_D$ of the Fermi surface, and an instability of the Fermi surface with respect to establishment of a highly ordered state, in which pairs of electrons are in a stable state. One of the quantitative consequences of this model is that the binding energy of electrons in this ground state, and also the transition temperature at which the pair condensation begins, should, for a given material, scale in proportion to the characteristic phonon frequency $\hbar\omega_D$, in the weak coupling regime. The prediction is that

$$k_B T_c = 1.13 \hbar\omega_D \exp[-1/N(0)V] \quad (4.1)$$

where $N(0)$ is the density of states for one spin at the Fermi level, and V is the average matrix element of the attractive interaction for energies within $\hbar\omega_D$ of the Fermi level.

This theoretical dependence of T_c on the average isotopic mass M , is derived from the fact that the energy $\hbar\omega_D$, should scale with $M^{-1/2}$. So far we can see that $T_c \propto \hbar\omega_D \propto M^{-1/2}$ with the theoretical value of α at 1/2. This has been tested experimentally for a number of elemental superconductors, some of which are listed in Table 6.

Table 6. Isotope effect in superconductors. Experimental values of α in $M^\alpha T_c = \text{constant}$, where M is the isotopic mass.

Substance	α	Substance	α
Zn	0.45 ± 0.05	Ru	0.00 ± 0.05
Cd	0.32 ± 0.07	Os	0.15 ± 0.05
Sn	0.47 ± 0.02	Mo	0.33
Hg	0.50 ± 0.03	Nb ₃ Sn	0.08 ± 0.02
Pb	0.49 ± 0.02	Zr	0.00 ± 0.05

Although the original BCS theory has gone far in explaining the isotope effect of superconductivity, there are some measurement that, by more elaborate experiments, showed that the isotope exponent, if indeed closed to the theoretical value of $1/2$, nevertheless deviated markedly from this value in a large number of materials. Many sophisticated calculations were made, attempting to account for the observed values of α .

The works of Swihart [80], Morel and Anderson [81], include the Coulomb repulsion between electron as well as the electron-phonon interaction used by BCS theory and do not cut the Coulomb repulsion arbitrarily at the Debye cut-off $\hbar\omega_D$, but rather at a much larger energy. The accounting for the Coulomb repulsion $V_c(q)$ extends the BCS gap equation by adding the repulsion interaction term. In the weak coupling limit, they obtained the gap equation in the form

$$\ln(2\omega_D/\Delta) = \left[\lambda - \frac{\mu}{1 + \mu \ln(E_F/\omega_D)} \right]^{-1} \quad (4.2)$$

where λ is the electron-phonon coupling and μ is the average Coulomb repulsion parameter given by

$$\mu = \frac{1}{4\pi^3 v_o} \int_0^{2k_o} \frac{4\pi e^2}{k_s^2 + q^2} q dq \quad (4.3)$$

where, v_o is the velocity of the electrons on the Fermi level, k_s is the screening Fermi momentum, and k_o is the Fermi momentum. The gap equation in Eq.(4.2) is in terms of

$$\Delta = 2\omega_D \exp \left[-\frac{1}{(\lambda - \mu^*)} \right] \quad (4.4)$$

where μ^* is

$$\mu^* = \frac{\mu}{1 + \mu \ln(E_F / \omega_D)} \quad (4.5)$$

The solution for the transition temperature is then in the order of

$$T_c \approx 1.14\theta_D \exp \left[-\frac{1}{(\lambda - \mu^*)} \right] \quad (4.6)$$

where θ_D is the Debye temperature.

The isotope effect concerns the dependence of the energy gap, Δ , upon the phonon energy $k_B\theta_D$. By differentiating (4.2) with respect to the phonon energy, we obtain the isotope exponent, approximately

$$\alpha = -\frac{(d\Delta/\Delta)}{(dM/M)} = \frac{1}{2} [1 - 0.01 (N(0)V)^{-2}] \quad (4.7)$$

Eq. (4.7) modifies the simple relation of T_c to isotope mass as predicted by BCS theory.

For the classical metal superconductors, the α obtained in Table 7, are calculated from Eq. (4.7). These results indicate a significant discrepancy from the BCS theoretical value and are in fairly good agreement with the observations.

Table 7. The Debye temperature and the critical temperature are taken from the "American Institute of Physics Handbook, " McGraw- Hill, 1957. $N(0)V$ is estimated from the critical temperature with the help of the BCS equation. The exponent of the isotope effect (last column) is derived from this experimental value of $N(0)V$ with the help of relation (4.7).

	$\theta_D(K)$	$T_c(K)$	λ	μ^*	$\lambda - \mu^*$	$N(0)V$	$-(d\Delta/\Delta)(dM/M)$
Na	160	...	0.25	0.12	0.13
K	100	...	0.25	0.12	0.13
Cu	343	...	0.20	0.10	0.10
Au	164	...	0.18	0.10	0.08
Mg	342	...	0.32	0.12	0.20
Ca	220	...	0.27	0.11	0.16
Zn	235	0.9	0.25	0.09	0.16	0.18	0.35
Cd	164	0.56	0.23	0.09	0.14	0.175	0.34
Hg	70	4.16	0.37	0.10	0.27	0.35	0.46
Al	375	1.2	0.33	0.10	0.23	0.175	0.34
In	109	3.4	0.34	0.10	0.24	0.29	0.44
Tl	100	2.4	0.32	0.09	0.23	0.27	0.43
Sn	195	3.75	0.34	0.10	0.24	0.25	0.42
Pb	96	7.22	0.40	0.10	0.30	0.39	0.47
Ti	430	0.4	0.41	0.11	0.30	0.14	0.25
Zr	265	0.55	0.37	0.11	0.26	0.16	0.30
V	338	4.9	0.47	0.12	0.35	0.24	0.41
Nb	320	8.8	0.47	0.12	0.35	0.32	0.45
Ta	230	4.4	0.45	0.11	0.34	0.25	0.42
Mo	360	...	0.38	0.10	0.28
U	200	1.1	0.47	0.12	0.35	0.19	0.36

Including the Coulomb repulsion term in the BCS theory is successful in explaining the deviation of the isotope exponent leading to the key point that any purely electronic pairing interaction between electrons in the BCS theory, whether repulsive or attractive, will cause an isotope exponent deviation. In other words, the discrepancy in the value shows that the simple phonon model must be generalized to account for

the electron-electron terms, but do not show the inapplicability of BCS theory. However, concerning the results of this formalism at higher temperatures, by use the fomulation $\alpha = - (d \ln T_c / d \ln M)$ with $\theta_D \approx M^{-1/2}$, we have calculated the α in term of the transition temperature, from Eq. (4.6) and obtain

$$\alpha = \frac{1}{2} \left\{ 1 - \left[1 + \lambda \ln \left(\frac{k_B T_c}{\hbar \omega_D} \right) \right] \right\} \quad (4.8).$$

The isotope effect exponent α is plotted with T_c are shown in Fig. 15. As the transition temperature increases, α takes negative values that are unphysical for the high- T_c copper oxide superconductors which we will see next.

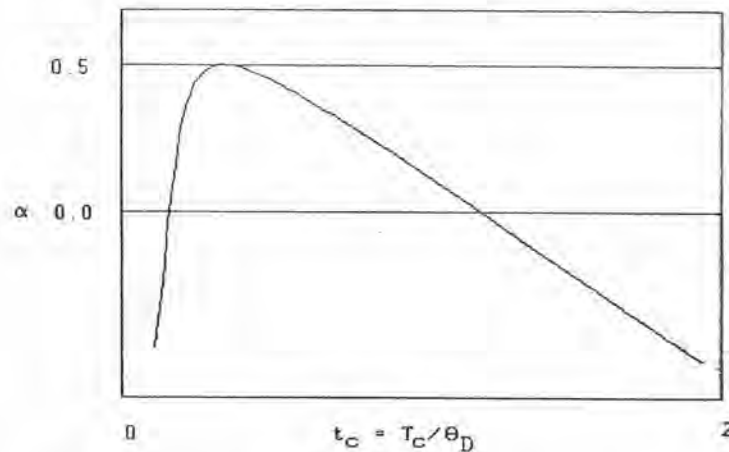


Fig. 15 The plot of α with T_c (from Morel and Anderson formulation[81]).

Strong-coupling Theory and the Isotope Exponent in Conventional Superconductors

Besides the BCS theory and the inclusion of the Coulomb repulsion term, much progress has been made in understanding the role of the electron-phonon interaction on the superconducting state and also their isotope effect phenomena. Another formula, the so called "strong-coupled" theory, has also given an excellent and comprehensive description of superconductivity. The strong-coupling superconductors, which occurs in classical metal superconductors such as Pb and Hg [82], show that the

electronic thermal conductivity differs markedly from that of typical weak superconductors like tin and indium. For lead and mercury the ratio, K_s / K_N , of the thermal conductivity in the superconducting stage and normal stage when plotted against the reduce temperature T / T_c shows a positive slope of about 5 near T_c , but a small slope about 1.6 in tin and indium. The theory of the electronic thermal conductivity of superconductors is based on the quasiparticle approximation and the Boltzmann equation gives the result which agree with the data on tin and indium, but not in Hg and Pb as Schrieffer, Scalapino, and Wilkins[83] have shown. That the strong-coupling cause the quasiparticle picture to be quite meaningless and it seems reasonable to study the thermal conductivity of Hg and Pb on the basis of the strong-coupling theory. Later others properties such as the tunneling characteristic[83], the transition temperature, and the isotope effect were investigated by McMillan[84].

McMillan worked on the framework of the strong-coupling formalism, using the Eliashburg equation[85]. He wrote down the integral equations for strong-coupling superconductors at the transition temperature. The normal and pairing self-energies are

$$\xi(\omega) = [1 - Z(\omega)] \omega \quad (4.9a)$$

$$\begin{aligned} &= \int_0^\infty d\omega' \int_0^{\omega_0} d\omega_q \alpha^2(\omega_q) F(\omega_q) \\ &\times \{ [N(\omega_q) + f(-\omega')] [(\omega' + \omega_q + \omega)^{-1} - (\omega' + \omega_q - \omega)^{-1}] \\ &+ [N(\omega_q) + f(\omega)] [(-\omega' + \omega_q + \omega)^{-1} - (-\omega' + \omega_q - \omega)^{-1}] \} \quad (4.9b) \end{aligned}$$

$$\Delta(\omega) = [Z(\omega)]^{-1} \int_0^\infty \frac{d\omega'}{\omega'} \times \text{Re}[\Delta(\omega')] \int_0^{\omega_0} d\omega_q \alpha^2(\omega_q) F(\omega_q)$$

$$\begin{aligned}
& \times \{ [N(\omega_q) + f(-\omega')] [(\omega' + \omega_q + \omega)^{-1} - (\omega' + \omega_q - \omega)^{-1}] \\
& - [N(\omega_q) + f(\omega)] [(-\omega' + \omega_q + \omega)^{-1} + (-\omega' + \omega_q - \omega)^{-1}] \} \\
& - \frac{N(0)V_c}{Z(\omega)} \int_0^{E_B} \frac{d\omega'}{\omega'} \times \text{Re}[\Delta(\omega')] [1 - 2f(\omega')]
\end{aligned} \tag{4.9c}$$

where $Z(\omega)$ is the renormalization parameter, $F(\omega_q)$ is the phonon density of states, ω_0 is the maximum phonon frequency, $\alpha^2(\omega_q)$ is the average of the electron-phonon interaction, V_c is the matrix element of the screened Coulomb interaction averaged over the Fermi surface, E_B is the electronic band width, and $N(\omega)$ and $f(\omega)$ are representatively the Bose and Fermi occupation probabilities. The screened Coulomb interaction is described by the parameters $N(0)V_c$ and E_B , and the electron-phonon interaction by the function $\alpha^2(\omega_q)F(\omega_q)$.

In order to solve the expressions (4.9b) and (4.9c) so as to get an accurate T_c , it is necessary to know the parameters $\alpha^2F(\omega_q)$ and $N(0)V_c$ (these microscopic parameters are known for many conventional superconductors from McMillan and Rowell [86] inversion of tunneling data). In trying to find an approximated solution to Eq. (4.9), McMillan substituted a trial function for $\Delta(\omega)$ on the right handside of Eq. (4.9). The trial function $\Delta(\omega)$ is chosen in the form

$$\Delta = \begin{cases} \Delta_0 & \text{if } 0 < \omega < \omega_D \\ \Delta_\infty & \text{if } \omega > \omega_D \end{cases} \tag{4.10}$$

Neglecting the thermal phonons, he found that the $\Delta(0)$ and $\Delta(\infty)$ are given as follows

$$\begin{aligned}
\Delta(0) &= \Delta_0 \\
&= [\Delta_0 \lambda / Z(0)] \ln (\omega_0 / T_c) + [\Delta_\infty / Z(0)] (\langle \omega \rangle / \omega_0) \lambda
\end{aligned}$$

$$- [N(0)V_c / Z(0)] [\Delta_0 \ln (\omega_0 / T_c)] + \Delta_\infty \ln (E_B / \omega_0) \quad (4.11)$$

$$\begin{aligned} \Delta(\infty) &= \Delta_\infty \\ &= -N(0) V_c [\Delta_0 \ln (\omega_0 / T_c) + \Delta_\infty \ln (E_B / \omega_0)] \\ &= \frac{N(0) V_c [\Delta_0 \ln (\omega_0 / T_c)]}{1 + N(0) V_c \ln (E_B / \omega_0)} \\ &= \mu^* \Delta_0 \ln (\omega_0 / T_c) \end{aligned} \quad (4.12)$$

where the μ^* is the Coulomb pseudopotential of Morel and Anderson,

$$\mu^* = \frac{\mu}{1 + \mu \ln(E_F / \omega_D)} \quad (4.13)$$

$\langle \omega \rangle$ is the average phonon frequency,

$$\langle \omega \rangle = \frac{\int_0^{\omega_0} d\omega_q \alpha^2(\omega_q) F(\omega_q)}{\int_0^{\omega_0} \frac{d\omega_q}{\omega_q} \alpha^2(\omega_q) F(\omega_q)} \quad (4.14)$$

and λ is an average electron-phonon interaction,

$$\lambda = \int_0^{\omega_0} \frac{d\omega_q}{\omega_q} \alpha^2(\omega_q) F(\omega_q) \quad (4.15)$$

Substituting Eq. (4.12) into Eq. (4.11), the strong-coupling formula gives the transition temperature as a function of the coupling constant for the electron-phonon and the Coulomb interaction in form

$$T_c = \omega_0 \exp \left[\frac{-(1+\lambda)}{\lambda - \mu^* - (\langle \omega \rangle / \omega_D) \lambda \mu^*} \right] \quad (4.16)$$

In order to find a more accurate solution of the transition temperature equation, McMillan tried to solve Eq. (4.9) by an iterating procedure by rewriting the equation in the form

$$\Delta_{n+1}(\omega) = \int d\omega' K(\omega, \omega') \Delta_n(\omega') \quad (4.17)$$

and choosing $\Delta_1(\omega)$ to be the initial choice in Eq. (4.9). He performed a numerical calculation for λ values for several values of T_c and μ^* with T_c in the range 0.001 K to 20 K and μ^* between 0 to 0.2. The results for λ for various values of T_c and μ^* are given in Table 8, and use Eq. (4.16) to fit the data. Firstly, a plot of $\ln(\theta_D / T_c)$, where θ_D is the Debye characteristic phonon frequency, versus $(1+\lambda)/\lambda$ for $\mu^* = 0$ yields a straightline (see Fig. 16a) with a slope of 1.04 and an intercept of 0.37 (equal to $\ln 1.45$). Then Eq. (4.16) becomes to

$$\ln \left(\frac{\theta_D}{T_c} \right) = 1.04 \left(\frac{1+\lambda}{\lambda} \right) + 0.37 \quad (4.18)$$

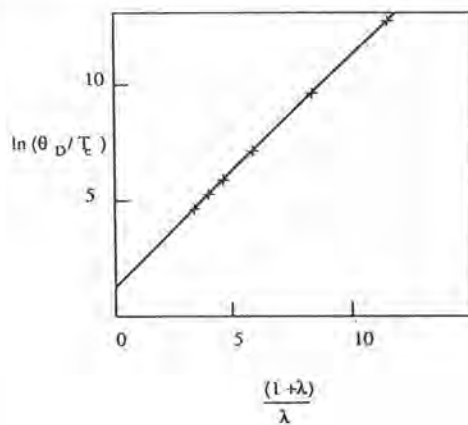
or

$$T_c = \frac{\theta_D}{1.45} \exp \left[-1.04 \left(\frac{1+\lambda}{\lambda} \right) \right] \quad (4.19)$$

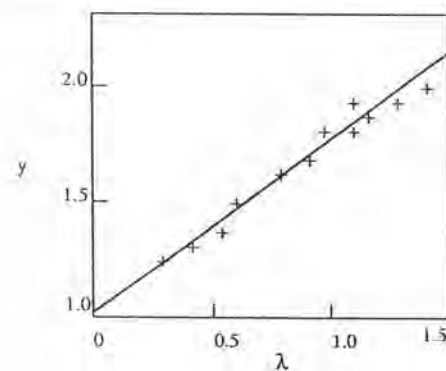
for $\mu^* = 0$. Secondly, for any μ^* , the plot of $y = 1 + (\langle \omega \rangle / \omega_0) \lambda$ versus $\frac{1}{\mu} \left(\lambda - \frac{1.04 (1 + \lambda) / \lambda}{\ln(\theta_D / 1.45 T_c)} \right)$ gives a straight line (see Fig. 16b) with a slope $\langle \omega \rangle / \omega_0 = 0.62$ and an intercept of 1 providing a good fit to the numerical data. The final formula for the transition temperature is then

Table 8 Values of the coupling constant λ for various values of the Coulomb terms μ^* and transition temperature T_c (K).

T_c	$\mu^* = 0$	0.088	0.149	0.157	0.243
20	0.85	1.12	1.34		
15	0.68	0.93	1.12		1.47
10	0.55	0.75	0.91		1.20
5	0.40	0.58		0.72	
1	0.25	0.39		0.50	
0.1	0.16	0.28		0.38	
0.001	0.09			0.25	



(16a)



(16b)

Fig. 16 The logarithm of θ_D versus $(1 + \lambda) / \lambda$ from a solution of the integral equation of the strong coupling theory for $\mu^* = 0$ (a) and the quantity y defined as $y = 1 + (\langle \omega \rangle / \omega_0) \lambda$ versus λ (b)

$$k_B T_c = \frac{\hbar \omega_D}{1.45} \exp \left[\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62)} \right] \quad (4.20)$$

which depends on μ^* . We can find the isotope exponent by using (4.20) and also the definition of $\alpha = -d(\ln T_c / \ln M)$ with the relation in $\hbar \omega_D \cong M^{-1/2}$. We obtain

$$\alpha = \frac{1}{2} \left\{ 1 - \left(\mu^* \ln \left(\frac{\hbar \omega_D}{1.45 k_B T_c} \right) \right) \frac{1 + 0.62\lambda}{1 + \lambda} \right\} \quad (4.21)$$

This formula has been popular and much more quantitative than the BCS result. In Eq. (4.21), α reduces to its ideal value 1/2 when $\mu^* = 0$, and is, general, less than this when μ^* is finite. A plot is given in Fig. 17 for α as a function of λ for three values of μ^* namely, $\mu^* = 0.1, 0.13$, and 0.2 .

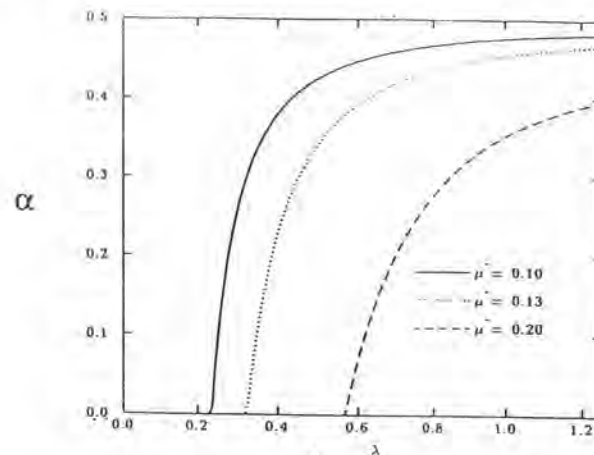


Fig. 17 Isotope effect coefficient α as a function of λ obtained from the McMillan equation for the three values of μ^* ($\mu^* = 0.1$, solid curve; $\mu^* = 0.13$ dotted curve; and $\mu^* = 0.2$, dashed curve).

It is clear that α is different from 1/2 when λ is small, in which case it can be negative when λ and μ^* are nearly balanced. When λ gets much larger than μ^* , which is expected for an electron-phonon system with large T_c , the isotope exponent will be

close to its ideal value. Further, Fig. 18 gives a plot of the α against T_c as Eq. (4.21). The lack of agreement of the data on the new oxide superconductors with the strong-coupling theory indicate a need to search for other theories.

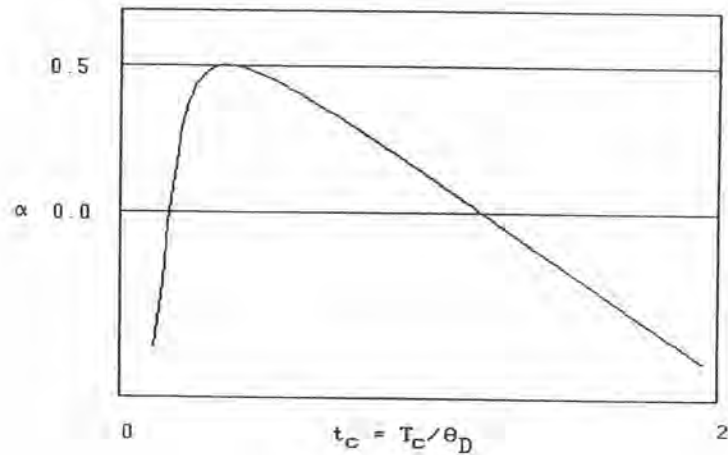


Fig. 18 The plot of α against T_c within the strong-coupling formulation

Isotope Effect in High Temperature Superconductors

For high temperature cuprates, that is copper oxide superconductors, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$, Bi-based and Tl-based, the isotope effect is studied by substitution of different atomic species in their components. Studies include partial substitution of O^{18} , Ba^{35} , Sr^{87} , La^{139} , Ba^{136} , Cu^{63} , or Cu^{65} . In several examples O^{18} substitution was studied in particular. The oxygen isotope effect in La-Sr-Cu-O appears to have first been reported by Battlogg and Cava[8] who find $\alpha_{\text{ox}} = 0.16 \pm 0.02$, and by Falten[9] with $\alpha_{\text{ox}} = 0.22$ and $\alpha_{\text{ox}} = 0.13$ in different samples. A subsequent determination by Bourne[10] reduces the uncertainty in previous work and finds $\alpha_{\text{ox}} = 0.14 \pm 0.08$, and zur Loye[11] quotes a value of $\alpha_{\text{ox}} = 0.31$.

In the Y-Ba-Cu-O system, α has been measure first by Battlogg, Kourouklis [12], and by Bourne, et. al. [13]. In The first paper, $\alpha_{\text{ox}} = 0.0 \pm 0.02$, while the second reports $\alpha_{\text{ox}} = 0.0 \pm 0.027$. Later, Lenry and some of the Berkeley group [14] gave a

finite $\alpha_{\text{ox}} = 0.05$. Another measurement by Morris[15] gave a change of critical temperature 0.019 ± 0.05 K for an 88 percent O^{18} substituted sample, and Benitez[16] found 0.16 ± 0.06 K for 90 percent O^{18} . A most recent publication by Yuon[17], found the change of the transition temperature to be 0.4 ± 0.1 K confirming the value of $\alpha_{\text{ox}} = 0.05$, and Hoen[18] give $\alpha_{\text{ox}} = 0.019 \pm 0.004$. For other partial isotope effects, Bourne and Zettl[18] consider both Cu and Ba substitutions and quote $\alpha_{\text{Cu}} = 0.0 \pm 0.07$ and $\alpha_{\text{Ba}} = 0.0 \pm 0.01$. Lin[19] finds no shift for Cu, while Vasilier and co-workers [20] find $\alpha_{\text{ox}} = 0.01 \pm 0.03$ and, finally, Hidaka [21] obtained zero for α_{Ba} in Y-Ba-Cu-O systems. Recently, in Bi-based Müller[22] gave $\alpha_{\text{ox}} = 0.04$ in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\alpha_{\text{ox}} = 0.12$ in $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$.

Further, there are observations of a strong dependence of the oxygen isotope effect on the doping level in a large number of the oxide superconductors. In $\text{La}_x\text{Sr}_{2-x}\text{CuO}_3$ Crawford et al. [23] found that for values of $x < 0.15$, α_{ox} is large in the range 0.4 to 0.6 but decreases by about a factor of 5 for $x > 0.15$ with $\alpha_{\text{ox}} \cong 0.1$. At $x = 0.11$ and 0.15 the α exceeds the BCS limit. For $\text{YBa}_2\text{Cu}_3\text{O}_7$, Bronemann and Morris [24] reported the dependence of the oxygen isotope effect shift on transition temperature within the La-doped system $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_7$. Recently, Frank et al. [25] substituted the rare earth ion Pr into the 91 K superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$, according to the formula $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_7$, leading to superconductors with substitution of $x = 0.2, 0.3,$ and 0.4 . It is found that the oxygen isotope exponent α_{ox} increases with increasing x and decreases transition temperature. For the highest Pr-doping, α_{ox} tends towards 0.5.

It seems clear from all of this that the isotope effect in oxide superconductors is small but measurable in a careful study using different methods of preparation and measurement. Clearly, the systematic change in oxygen isotope shift with doping of various ions, the anomalous effect where α exceeds 1/2 in $\text{La}_x\text{Sr}_{2-x}\text{CuO}_3$ and the

small value α_{ox} in these new oxide superconductors are rich source of information and may help to sort out theories.

The Oxygen Isotope Effect and Apex Anharmonicity [22]

Even the simplest formula (4.1) of BCS theory are written in the form

$$k_B T_c = 1.13 \hbar \omega_D \exp[-1/N(0)V] \quad (4.22)$$

allows us to elucidate the main factors which can lead to an increase in T_c . Apparently, these factors are an increase in the width of the characteristic interaction region θ_D , the density of states, $N(0)$, on the Fermi boundary and the interaction V responsible for pairing. For the case of the pair interaction, Müller[22] assumes only the anharmonic motion of the ions to be relevant for superconductivity. He was mainly interested in the percentage of anharmonic motion of the apex O(4), which acts as the source for enhancing the paired interaction V , and he conjectured that part of the dynamic yields an isotope effect which is roughly proportionality to the apex oxygen percent in the unit cell of perovskite copper oxide superconductors.

Müller has discussed this relation for various compounds. For La-Sr-Cu-O, the oxygen isotope effect is observed with $\alpha_{\text{ox}} = 0.13$ and 0.16 . For the apex motion alone, $1/2$ of the total $\alpha_{\text{ox}} = 0.5$, i. e., 0.25 is expected and compared to the experimental values. Conversely, he used this data to introduce the relation

$$\alpha_a = \alpha_o / r \quad (4.23)$$

where α_a is for the apex oxygen and r is the ratio of the apex oxygen per total oxygen per unit cell. Values obtained from this relation range from 0.26 to 0.32 . From these numbers Müller suggest that, if this anharmonic motion is important, one either is in a strong-coupling regime or there is another mechanism for superconductivity present.

In $\text{YBa}_2\text{Cu}_3\text{O}_7$ and its rare-earth isomorphs, the ratio of an apex and total oxygen is $2/7$ and, using an isotope effect shift from both [23] and [24] which is nearly constant, one obtains an α_a of 0.14 and 0.06. So far, he expected a measured isotope effect in $\text{YBa}_2\text{Cu}_4\text{O}_8$ not much smaller and α_a essentially the same value as in $\text{YBa}_2\text{Cu}_3\text{O}_7$ with r equal to $2/8$ (It would be of substantial value to know the isotope effect exponent for $\text{YBa}_2\text{Cu}_3\text{O}_8$). Consequently, the relative number of apex oxygen atoms is quite small, ranging from $1/3$ for $n = 1$ (copper-oxide layer) in Bi-based to $r = 1/6$ for $n = 4$ in Tl-based. It would be regarding to measure the isotope shift because it should decrease by factor of two in going from the $n = 1$ to $n = 4$. A list of the ratios, r , in the selected compounds are shown in Table 9, and in Table 8 the evaluated α_a according to Eq. (4.23). However, the formulation of this anharmonicity is necessary for further studies. The α_a that are given in Table 10 might be fortuitous and have to await experimental measurements proposed. We need to achieve progress in understanding Eq. (4.23).

Table 9 Evaluation of the apex oxygen to the total oxygen ions ratio.

Compound	Layer	Oxygen per layer	Apex oxygen	Ratio apex / total
$\text{YBa}_2\text{Cu}_3\text{O}_7$	CuO	1	1	$2/7$
	BaO	1		
	CuO_2	2		
	Y	-		
	CuO_2	2		
	BaO	1		
$\text{YBa}_2\text{Cu}_4\text{O}_8$	CuO	1	1	$2/8$
	CuO	1		
	BaO	1		
	CuO_2	2		
	Y	-		
	CuO_2	1		
	BaO	1		
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$ $n = 1$ also $\text{Tl}_2\text{Ba}_2\text{CuO}_6$	Bi_2O_2	2	1	
	SrO	1		
	CuO_2	2		

	SrO	1	1	1/3
Bi ₂ Sr ₂ CaCu ₂ O ₈ n = 2 also	Bi ₂ O ₂	2		
Tl ₂ Ba ₂ CaCu ₂ O ₈	(Ca, Sr)O	1	1	
	CuO ₂	2		
	(Ca, Sr)	-		
	CuO ₂	2		
	(Ca, Sr)O	1	1	1/4
Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀ n = 3 also	Bi ₂ O ₂	2		
Tl ₂ Ba ₂ Ca ₂ Cu ₃ O ₁₀	SrO	1	1	
	CuO ₂	2		
	Ca	-		
	CuO ₂	2		
	Ca	-		
	CuO ₂	2		
	SrO	1	1	1/5
Bi ₂ Sr ₂ Ca ₃ Cu ₄ O ₁₂ n = 4		12	2	1/6
TlBa ₂ CuO ₅ n = 1	TlO	1		
	BaO	1	1	
	CuO ₂	2		
	BaO	1	1	2/5
TlCaBa ₂ Cu ₂ O ₇ n = 2	TlO	1		
	BaO	1	1	
	CuO ₂	2		
	CaO	1		
	CuO ₂	2		
	BaO	1	1	2/7
TlCa ₂ Ba ₂ Cu ₃ O ₉ n = 3		9	2	2/9
TlCa ₃ Ba ₂ Cu ₄ O ₁₁ n = 4		11	2	2/11

Table 10 Measured oxygen isotope shifts for O¹⁸ substitution for O¹⁶, δT_c calculated oxygen isotope shift exponent using Eq. (4.22) and the apex oxygen shift α using Eq. (4.23).

Compound	Reference	T_c (K)	δT_c (K)	α_o	α_a
La ₂ CuO ₄	17, 18	38		0.31- 0.16	0.26 - 0.32
YBa ₂ Cu ₃ O ₇	23	91	0.46	0.040	0.14
YBa ₂ Cu ₃ O ₇	24	91	0.20	0.018	0.06
Bi ₂ Sr ₂ CaCu ₃ O ₈		75	0.32	0.034	0.14
Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀		110	0.34	0.023	0.12

The Importance of Some Electronic Interactions for the Isotope Effect in Higher Critical Temperature Superconductors

According to the calculation by Swihart [80] and by Morel and Anderson [81] which includes the Coulomb interaction as well as the electron-phonon interaction in the BCS theory, a deviation of the isotope effect from the ideal $\alpha = 1/2$ value is in fairly good agreement with the observations in the conventional superconductors. On this basis Daemen and Overhauser[29] try to extend the BCS theory for use in the high transition temperature cuprates by using a simple two square-well interaction from for any of the interactions responsible for superconductivity. The model of interaction is given by the expression

$$V_{kk'} = \begin{cases} -(V_1 + V_2) & \text{if } |\xi_k| < \hbar\omega_D, |\xi_{k'}| < \hbar\omega_D \\ -V_2 & \text{if } \hbar\omega_D < |\xi_k| < E_c, \hbar\omega_D < |\xi_{k'}| < E_c \end{cases} \quad (4.24)$$

where V_1 is the phonon-mediated interaction, V_2 is any short-range interaction, ξ_k is the electron energy measured with respect to the Fermi energy and E_c is the energy cut off for V_2 . According to the simple form of the interaction in the Eq. (4.24), one looks for a solution of the BCS gap equation of the form

$$\begin{aligned} \Delta(k, T) &= \Delta_0(T)\Delta_1 & \text{if } |\xi_k, \xi_{k'}| < \hbar\omega_D \\ &= \Delta_0(T)\Delta_2 & \text{if } \hbar\omega_D < |\xi_k, \xi_{k'}| < E_c \end{aligned} \quad (4.25)$$

and substitute this condition in the BCS gap equation and obtain the following solution for Δ_1 and Δ_2

$$\begin{aligned} \Delta_1 &= (V_1 + V_2)\Delta_1\Sigma_1 + V_2\Delta_2\Sigma_2 \\ \Delta_2 &= V_2\Delta_1\Sigma_1 + V_2\Delta_2\Sigma_2 \end{aligned} \quad (4.26)$$

Σ_1 and Σ_2 are defined as

$$\Sigma_1 = \int_0^{\hbar\omega_D} d\xi N(\xi) \frac{1}{\sqrt{\xi_{k'}^2 + \Delta_1^2(T)}} \tanh \frac{\sqrt{\xi_{k'}^2 + \Delta_1^2(T)}}{2k_B T} \quad (4.27)$$

$$\Sigma_2 = \int_{\hbar\omega_D}^{E_c} d\xi N(\xi) \frac{1}{\sqrt{\xi_{k'}^2 + \Delta_2^2(T)}} \tanh \frac{\sqrt{\xi_{k'}^2 + \Delta_2^2(T)}}{2k_B T} \quad (4.28)$$

with $N(0)$ being the electronic density of states at the Fermi level. $N(0)$ is defined as a constant.

At the transition temperature $\Delta_0(T)$ goes to zero and Eq. (4.26) and leads to the expression

$$1 - \lambda F\left(\frac{\hbar\omega_D}{k_B T_c}\right) - \sigma F\left(\frac{E_c}{k_B T_c}\right) - \lambda\sigma \left[F\left(\frac{\hbar\omega_D}{k_B T_c}\right)\right]^2 + \lambda\sigma F\left(\frac{\hbar\omega_D}{k_B T_c}\right) F\left(\frac{E_c}{k_B T_c}\right) = 0 \quad (4.29)$$

where

$$F(x) = \int_0^{x/2} dz \frac{\tanh(z)}{z} \ln\left[\frac{E_F}{2zk_B T_c}\right] \quad (4.30)$$

with $\lambda = N(0)V_1$ and $\sigma = N(0)V_2$.

Assuming that $k_B T_c$ is much less than both $\hbar\omega_D$ and E_c , $F(x)$ is approximated by $\ln(1.14x)$ and Eq.(4.29) becomes to

$$1 - \lambda \ln(1.14 \hbar\omega / k_B T_c) - \sigma \ln(1.14 E_c / k_B T_c) - \lambda\sigma [\ln(1.14 \hbar\omega / k_B T_c)]^2 + \lambda\sigma [\ln(1.14 \hbar\omega / k_B T_c)] [\ln(1.14 E_c / k_B T_c)] = 0 \quad (4.31)$$

After some algebraic steps they get the same expression as Morel and Anderson ;

$$k_B T_c = 1.14 \hbar\omega_D \exp\left[\frac{-1}{\lambda + \sigma^*}\right] \quad (4.32)$$

where

$$\sigma^* = \frac{\sigma}{1 - \sigma \ln(E_c / \hbar\omega_D)} \quad (4.33)$$

From Eq. (4.33), they obtain the isotope effect exponent

$$\alpha = \frac{1}{2} \{ 1 - [1 + \lambda \ln (k_B T_c / 1.14 \hbar \omega_D)] \} \quad (4.34)$$

The exact calculation for α can proceed from Eq. (4.29). By differentiating this equation with respect to M and using the definition

$$\alpha \equiv - \frac{M}{T_c} \frac{dT_c}{dM} \quad (4.35)$$

we have

$$\begin{aligned} & \frac{\lambda \hbar \omega_D}{M k_B T_c} \left(\frac{1}{2} - \alpha \right) F' \left(\frac{\hbar \omega_D}{k_B T_c} \right) - \frac{\sigma E_c \alpha}{M k_B T_c} F' \left(\frac{E_c}{k_B T_c} \right) - \lambda \sigma \frac{\hbar \omega_D}{M k_B T_c} \left(\frac{1}{2} - \alpha \right) \frac{E_c \alpha}{M k_B T_c} F' \left(\frac{\hbar \omega_D}{k_B T_c} \right) F' \left(\frac{E_c}{k_B T_c} \right) \\ & + \left[\lambda \sigma \frac{\hbar \omega_D}{M k_B T_c} \left(\frac{1}{2} - \alpha \right) F' \left(\frac{\hbar \omega_D}{k_B T_c} \right) \right] = 0 \end{aligned} \quad (4.36)$$

$$\text{with} \quad F'(x) = \frac{\tanh(x/2)}{x} \quad (4.37)$$

Finally, the result of the exact calculation gives α as

$$\alpha = \frac{1}{2} \left[1 + \left\{ \frac{\tanh(E_c / 2 \hbar \omega_D t_c)}{\tanh(1/t_c)} \right\} \left\{ \frac{[1 - \lambda F(1/t_c)]^2}{1 - [1 - \lambda F(1/t_c)]^2} \right\} \right]^{-1} \quad (4.38)$$

where $t_c = T_c / \theta_D$ and the critical temperature T_c is measured in units of θ_D (the Debye temperature).

Fig. 19 shows α as obtained from Eq.(4.38) which is plotted versus t_c for different values of λ . All curves show that α approaches zero at higher temperatures.

This vanishing of the isotope effect compares well with the experiments in high- T_c oxide superconductors. The effectiveness of this model is that it gives α for the selected high- T_c materials if we can find a favorable value of the λ parameter and choose the best function for the density of states $N(\xi)$ which we will present in the next chapter.

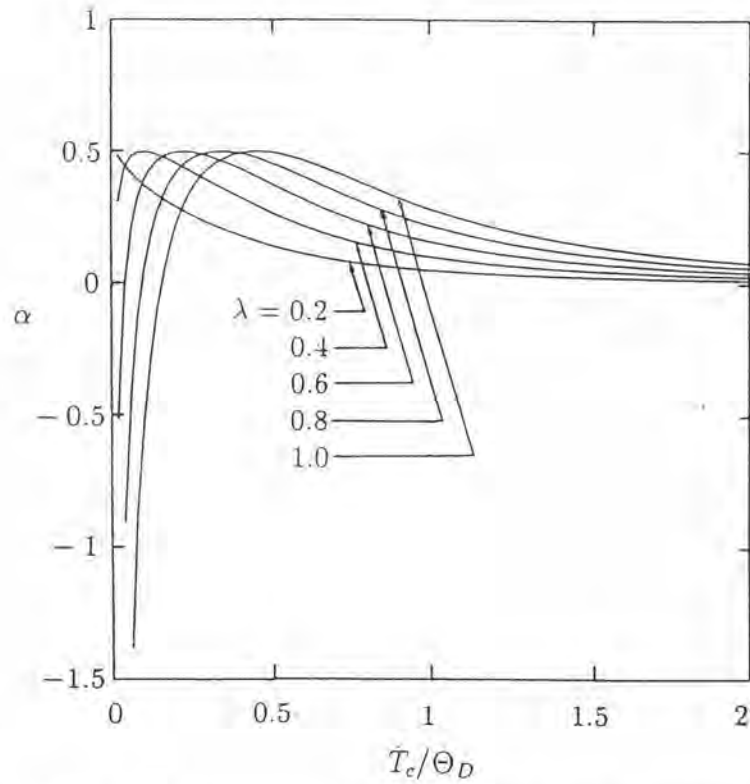


Fig. 19 The plot of α versus t_c , from Daemen and Overhauser work [29].