Strong-Coupling Superconductors, the Mössbauer Effect, and Localized Impurity Modes*

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McMillan has recently proposed that in the strong-coupling theory of superconductivity certain expectation values for the lattice eigenfrequencies play a dominant role. We point out here that the Mössbauer effect can measure the important parameter in McMillan's theory in a rather direct fashion. Local-impurity-model calculations assuming isotopic impurities are presented, suggesting that McMillan's parameter is locally enhanced by heavy impurities in light lattices.

I. INTRODUCTION

RECENTLY McMillan[1] has calculated the transition temperature for strong-coupling superconductors. He finds that for particular classes of materials the electron-phonon coupling constant is relatively independent of the electronic properties (in contrast to the weak-coupled case) and is therefore dependent on the phonon factors. He has supported this conjecture with data from the 5*d* transition-series elements. Further experimental study of this problem will require development of techniques which are capable of measuring the relevant lattice-stiffness parameters with precision.

We emphasize here (a) that the Mössbauer technique provides a particularly direct method of determining McMillan's parameter, a characteristic phonon frequency, for many situations, (b) that heavy impurities in light-host lattices can increase McMillan's parameter locally, and (c) that theories of the behavior of impurity atoms developed for the Mössbauer effect are useful in estimating the effect of the impurity on McMillan's parameter and also in interpreting the Mössbauer measurements of this parameter. Our analysis is based on a theory of isotopic impurities by Dawber and Elliott.[2] This theory assumes isotopic impurities only, i.e., force constants are not permitted to vary.

II. McMILLAN'S THEORY

McMillan derives expressions for the transition temperature of strong-coupling superconductors based upon the theory of Eliashberg.[3] A central conclusion of the paper is that for large classes of materials the transition temperature may be represented in a rather simple form:

$$T_c=\frac{\hbar\langle\omega\rangle}{0.544k}\exp\left(\frac{-1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right). \tag{1}$$

Here μ^* is the Coulomb pseudopotential and λ is the electron-phonon coupling constant; k and $\hbar$ have their usual meanings. On the Debye model the preexponential term is $\Theta/1.45$. An analysis of a number of transition metals and alloys leads McMillan to conclude that the electron-phonon coupling constant depends primarily upon phonon frequencies, rather than upon electron properties of the metal. In the following discussion we assume this point and investigate how the Mössbauer technique permits a rather direct determination of the relevant averages over the phonon spectrum.

The electron-phonon coupling constant is defined by McMillan as

$$\lambda\equiv 2\int_0^{\omega_0}\alpha^2(\omega)g(\omega)\frac{d\omega}{\omega}, \tag{2}$$

where $\alpha^2(\omega)$ is the average dynamic electron-phonon interaction, $g(\omega)$ is the phonon density of states, and ω_0 is the maximum phonon frequency. In the BCS theory[3,4] λ is approximately $N(0)V$ where $N(0)$ is the density of electronic states at the Fermi surface and V is the Cooper pairing potential due to $\alpha^2(\omega)$. In the strong-coupling theory McMillan finds

$$\lambda=\frac{N(0)\langle I^2\rangle}{M}\left(\int\alpha^2(\omega)g(\omega)\frac{d\omega}{\omega}\Big/\int\alpha^2(\omega)g(\omega)\omega\,d\omega\right), \tag{3}$$

where $\langle I^2\rangle$ is the average over the Fermi surface of the square of the electronic-matrix element of the change in the crystal potential when one atom is displaced, and M is the atomic mass.

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[1] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[2] R. J. Elliott, in *Phonons in Perfect Lattices and Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Oliver and Boyd, Edinburgh/London, 1966), Chap. 14. A factor ϵ should appear squared in many of the equations here which pertain to the local mode. See also P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **273**, 222 (1963).

[3] J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964).

[4] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 162 (1957); **108**, 1175 (1957).

Assuming, as McMillan has, that $\alpha^2(\omega)$ is frequency-independent, we can write

$$\lambda=\frac{N(0)\langle I^2\rangle}{M}\Big/(\langle\omega\rangle/\langle\omega^{-1}\rangle)_0, \tag{4}$$

where we have introduced the expectation values

$$\langle\omega^l\rangle_T=\int(\bar{n}+\tfrac{1}{2})g(\omega)\omega^l d\omega, \tag{5}$$

where $\bar{n}$ is the Bose occupation number. The subscript (0) in Eq. (4) indicates the ratio $\langle\omega\rangle/\langle\omega^{-1}\rangle$ is evaluated near $T=0$.

The connection with the Mössbauer effect arises from the fact that the second-order Doppler shift of the Mössbauer resonance is proportional to $\langle\omega\rangle$, while the logarithm of the Mössbauer recoil-free fraction f is proportional to $\langle\omega^{-1}\rangle$. While both of these quantities exhibit large temperature dependences, it has been shown experimentally that the ratio $\langle\omega\rangle/\langle\omega^{-1}\rangle$ is practically temperature-independent.[5] Thus, rather precise values of $(\langle\omega\rangle/\langle\omega^{-1}\rangle)_0$ can be easily obtained from the method discussed in Ref. 5. Another useful characteristic of the Mössbauer effect is that it permits the lattice properties of isolated impurity atoms to be studied. For reasons of experimental simplicity most Mössbauer studies have involved either Fe^{57} or Sn^{119} as impurities in various host lattices. The observed shifts and recoil-free fractions are properties of the impurity within the particular host lattice rather than properties of the pure host itself. We have previously[5] summarized some observed values of the ratio $(\langle\omega\rangle/\langle\omega^{-1}\rangle)_0$ obtained from Mössbauer experiments in terms of a temperature ψ_0 defined by

$$k^2\psi_0^2\equiv\hbar^2(\langle\omega\rangle/\langle\omega^{-1}\rangle)_0. \tag{6}$$

Within the Debye model $\psi_0=\Theta/\sqrt{2}$, while in the Einstein[6] model $\psi_0=\Theta_E$. We can compare directly ψ_0 with the McMillan parameter $\langle\omega^2\rangle^{1/2}(°K)$ as given in his Table VII. As yet there do not exist sufficient Mössbauer data to permit detailed conclusions. In particular, there is no overlap with McMillan's Table VII with the exception of recent Mössbauer measurements on Fe in Mo which yield a value of $\psi_0=271°K$, in good agreement with McMillan's value of 310°K (KCT of Ref. 5).

In the empirical study of superconductivity it is found that certain lattice structures (notably β-tungsten) are especially favorable to high transition temperatures. If the parameter $(\langle\omega\rangle/\langle\omega^{-1}\rangle)_0$ should also play a role, it becomes desirable to investigate methods of independently changing it. One such method may be the use of impurity systems.

[5] R. D. Taylor and P. P. Craig, Phys. Rev. **175**, 782 (1968); T. A. Kitchens, P. P. Craig, and R. D. Taylor (unpublished).
[6] W. M. Visscher, Phys. Rev. **129**, 28 (1963).

III. CALCULATIONS FOR ISOTOPIC IMPURITIES

A good deal of theoretical effort has been devoted to the analysis of vibrational modes of impurity atoms. Major contributors to this area include Visscher,[6] Kagan,[7] Maradudin and Flinn,[8] Pathak and Deo,[9] Elliott,[2] Housley and Hess,[10] and Dash *et al.*[11] The effects of changes in mass, changes in potentials, and of anharmonic forces have been investigated by these authors. To provide an indication of the type of effect expected upon the ratio $(\langle\omega\rangle/\langle\omega^{-1}\rangle)_0$, we have used the mass impurity calculation of Elliott.[2] His theory is exact for mass impurities of any magnitude. It assumes the harmonic interatomic potential to be unchanged by the presence of a mass discrepancy.

According to the calculation of Elliott,[2] for an impurity-to-host mass ratio $R=M'/M$,

$$\langle\omega^l\rangle=\int\left\{\omega^l g(\omega)(\bar{n}+\tfrac{1}{2})d\omega\Big/\left[\left(1+(1-R)^2\omega P\int\frac{g(\omega')d\omega'}{\omega^2-\omega'^2}\right)^2+[\tfrac{1}{2}\pi(1-R)\omega g(\omega)]^2\right]\right\}, \tag{7}$$

with an additional term on the right-hand side due to the local mode, if it exists. This term is

$$\Omega^{l-2}[\bar{n}(\Omega)+\tfrac{1}{2}]\left[(1-R)^2\int\frac{\omega'^2 g(\omega')d\omega'}{(\Omega^2-\omega'^2)^2}\right]^{-1}, \tag{8}$$

where Ω, the frequency of the local mode, is the eigenvalue of the equation

$$1-(1-R)\omega^2 P\int\frac{g(\omega')d\omega'}{\omega^2-\omega'^2}=0, \tag{9}$$

and where P indicates the principal value of the integral. In general, the local mode exists only for $R=M'/M$ less than some critical value R_c. For the Debye model, $R_c=1$.

We have evaluated these integrals on a computer for a variety of phonon spectra. Our procedure was to use numerical values of the assumed phonon spectra to compute the integral in Eq. (9) for a wide range of values for Ω and to tabulate the result, as shown in Fig. 1. With the aid of this table a search was made for each value of the host-to-impurity mass ratio in order to see if Eq. (9) had a solution. The final step was to evaluate Eq. (7) (which utilizes the tabulated integrals) and to add the contribution due to Eq. (8).

[7] Yu. Kagan, Zh. Eksperim. i Teor. Fiz. **47**, 366 (1964) [English transl.: Soviet Phys.—JETP **20**, 243 (1965)].
[8] A. A. Maradudin and P. A. Flinn, Phys. Rev. **126**, 2059 (1962).
[9] K. N. Pathak and B. Deo, Physica **35**, 167 (1967).
[10] R. M. Housley and F. Hess, Phys. Rev. **146**, 517 (1966).
[11] J. G. Dash, D. P. Johnson, and W. M. Visscher, Phys. Rev. **168**, 1087 (1968).

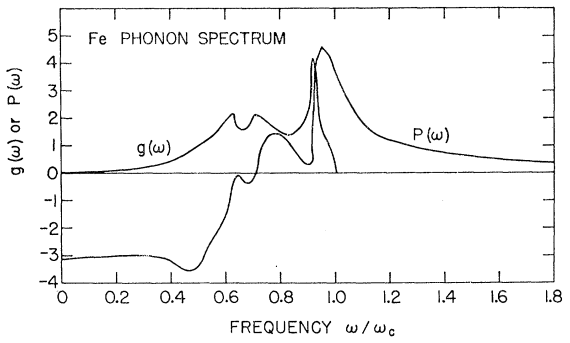

FIG. 1. The phonon density $g(\omega)$ for Fe from inelastic neutron scattering experiments of Minkiewicz *et al.* (Ref. 12) in unnormalized form and the principle-value integral $P(\omega)$ of Eq. (9).

The results shown in Fig. 2 are expressed as ratios

$$\frac{2R}{\omega_D^2}\frac{\langle\omega\rangle}{\langle\omega^{-1}\rangle}$$

evaluated at $T=0$ and at $T\to\infty$. The factor R is included because of a suggestion by Visscher that the effective Debye frequency of the impurity is $\omega_D/\sqrt{R}$, where ω_D is the Debye frequency of the host. This suggestion is borne out well by our calculations. The factor 2 normalizes the results to unity at $R=1$ on the Debye model.

The phonon spectra studied include:

(a) the Debye spectrum, $g(\omega)\sim\omega^2$,

(b) the experimentally observed Fe spectrum,[12] as determined from neutron diffraction, and

(c) a Debye spectrum rounded on the end by letting

$$g(\omega)\sim(\omega-\omega_D)^{1/2} \quad \text{for } \omega>0.75\omega_D.$$

At high temperatures equipartition of energy between kinetic and potential energy guarantees that the ratio $\langle\omega\rangle/\langle\omega^{-1}\rangle_\infty$ is independent of R and temperature. The numbers next to the curves give this ratio for the high-temperature limit for the various phonon spectra. In the low-temperature limit the curves may be rather well-represented straight lines on a semilog graph. The slope of the curves is remarkably insensitive to the particular form of the phonon spectra used.

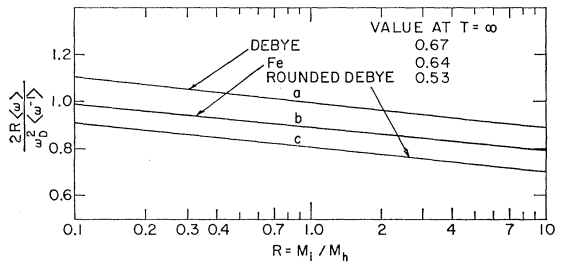

FIG. 2. Variation of the expectation value of the impurity frequency divided by the expectation value of the inverse impurity frequency (which is proportional to the electron-phonon factor) normalized to unity for a pure Debye lattice, as a function of the ratio R of the impurity mass to the host-lattice mass. The calculations are based on the theory of Dawber and Elliott (Ref. 2) for isotopic impurities and are performed for several phonon spectra. A remarkable feature of the calculations is the constancy of the slope of the curves.

[12] V. J. Minkiewicz, G. Shirane, and R. Nathans, Phys. Rev. **162**, 528 (1967).

We have computed curves similar to Fig. 2 for a number of other phonon spectra, both realistic and reasonable artificial ones. In all cases we find the slope to be approximately equal to that in the curves shown. In artificial spectra in which most of the density of states is concentrated into very low-frequency modes, it is possible to obtain values for the curves substantially below those shown, but the slopes are negligibly affected. In investigating the effect of various possible phonon spectra, it should be noted that only spectra rising at least linearly in ω in the low-frequency limit are permissible, for otherwise $\langle\omega^{-1}\rangle$ diverges.

The calculation allows only for isotopic impurities and does not permit changes in force constant.[2,6] Despite these restrictions, it is of interest to investigate whether the results displayed in Fig. 2 can be correlated with experimental results on superconductivity. In Sec. IV an attempt is made to establish such a correlation.

IV. ESTIMATE OF SHIFTS IN TRANSITION TEMPERATURES IN ALLOYS

The central results of McMillan's work are a simple expression [Eq. (1)] for the transition temperature of strong-coupled superconductors and the conclusion that lattice properties play a central role in determining T_c. In applying Eq. (1) to experimental values of T_c, McMillan finds that the Coulomb pseudopotential is approximately constant at about 0.13 ± 0.03.

We assume for the present that near an impurity the value of the electron-phonon coupling constant λ is altered, and that its variation is exclusively through the effect of impurity modes. We then define a local impurity value of λ,

$$\lambda_i=\frac{N(0)\langle I^2\rangle}{M_i(\langle\omega_i\rangle/\langle\omega_i^{-1}\rangle)_0}. \tag{10}$$

For isotopic impurities we have, using Eqs. (4) and (10),

$$\frac{\lambda}{\lambda_i}=R\frac{(\langle\omega_i\rangle/\langle\omega_i\rangle^{-1})_0}{(\langle\omega\rangle/\langle\omega^{-1}\rangle)_0}=\frac{2R}{\omega_D^2}(\langle\omega_i\rangle/\langle\omega_i^{-1}\rangle)_0. \tag{11}$$

The equation on the right is obtained by assuming a Debye model for the host lattice. With this assumption the form on the right is that plotted in Fig. 2, and we thus obtain a relation between λ and λ_i.

We can now define a local value T_{ci} for the transition

temperature in terms of Eqs. (1), (4), and (10):

$$\frac{T_{ci}}{T_c}=\frac{\langle\omega_i\rangle}{\langle\omega\rangle}\exp\left[\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\times\left(1-\frac{(1+\lambda_i)}{(1+\lambda)}\frac{[\lambda-\mu^*(1+0.62\lambda)]}{[\lambda_i-\mu_i^*(1+0.62\lambda_i)]}\right)\right]. \quad (12)$$

We have placed a subscript on the Coulomb pseudopotential μ_i^* as well as on λ_i for the impurity site. The calculated curves are very sensitive to slight changes in all these parameters.

From Fig. 2 one sees that the slope of the curves is approximately constant. We may analytically represent Fig. 2 by

$$\frac{\lambda}{\lambda_i}=\frac{2R\langle\omega_i\rangle}{\omega_0^2\langle\omega_i^{-1}\rangle}=c-0.133\log_{10}R, \quad (13)$$

where c is a constant equal to unity on the Debye model. For other typical phonon spectra c varies from unity by about 0.2. The data from Table I of Ref. 5 permit estimation of values of λ/λ_i for several values of R. It is found that there is considerable spread in the points, but that if the form of Eq. (13) is to be retained, a value of $c\sim0.6$ is required for Fe impurity data. This value is substantially below that obtained from computation using any except exceedingly unrealistic phonon spectra. It must be concluded, therefore, that Fe impurities in the various host lattices studied are strongly affected by force-constant changes, which are difficult to estimate, as well as by mass changes, which we have considered. Nonetheless, in applying Eq. (13) it would appear that a choice of $c=0.6$ is more in accord with experiment than is unity.

It is not obvious how to relate local shifts in transition temperature as given by Eq. (12) to bulk effects. The proper expression would involve the impurity concentration and might involve some weighting parameters such as the range over which the impurity influences the lattice modes or the electronic-pair correlation length. A plausible approximation would appear to be to assume the fractional shift in the bulk-observable-transition temperature is proportional to the fractional shift in local-transition temperature, multiplied by the concentration

$$\left(\frac{\delta T_c}{T_c}\right)_{\text{system}}=\beta x\left(\frac{\delta T_c}{T_c}\right)_{\text{local}}=\beta x\left(\frac{T_{ci}}{T_c}-1\right). \quad (14)$$

Here β is a proportionality constant. We have analyzed the transition-temperature-shift data of Chanin, Lynton, and Serin[13] in terms of variation with R. We find a general consistency in that the transition temperatures are found to decrease with increasing R. Typical shifts are of order

$$-0.6<\frac{\partial\delta T_c/T_c}{\partial x}(\%^{-1})<0,$$

where the value zero is typical of $R=1$ and the value -0.6 is typical of $R=4$. Computations using Eqs. (12)–(14) and typical values for the other parameters taken from McMillan yield agreement only if the parameter β in Eq. (14) is about 100. If we interpret β as the number of atomic volumes affected by the mass impurity and assume it to be 100, then we find good agreement with the Al and In alloy results of Chanin *et al.*[13] by letting $\lambda=0.38$, $\mu^*=0.130$, and $\mu_i^*=0.142$. This is equivalent to assuming an effective range of the mass impurity of 7 Å in these alloys. The agreement may be fortuitous because we have not properly included the effect of many factors normally considered important in dirty superconductors.[14,15]

V. CONCLUSION

The Mössbauer technique is found to offer a tool for investigating a critical parameter in McMillan's theory of superconductivity for the special case of impurities. Calculations of the expected behavior of isotopic impurities are made using the theory of Elliott[2] and are compared to experiment. Observed transition temperature shifts can be explained in terms of isotopic mass impurities without allowing for changes in force constants, Coulomb pseudopotential, or other parameters usually considered important in the problem. Whether the agreement is of significance, or is merely fortuitous, we cannot say.

ACKNOWLEDGMENTS

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