

and the generally decreasing atomic volume. We may speculate as to whether the tighter binding in the case of Gd is primarily to be associated with its ferromagnetism. A determination of the characteristic temperature of Lu will thus be of interest.

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The Isotope Effect in Superconductivity

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The isotope effect in superconductors is usually summarized by giving the observed values of p in the equation $M^p T_c = \text{constant}$, where M is the isotopic mass and T_c the superconducting transition temperature. Fröhlich predicted the value $p=1/2$, but the measurements in some instances show deviations from this prediction. An explanation of the deviation of p from $1/2$ is offered based on an analog of Wien's displacement law applicable to the vibration spectrum of real crystal lattices. The departure of p from the value $1/2$ is attributed to the departure of the frequency spectrum from a simple power law. For many superconducting elements, p may be estimated from specific heat data, when such data are available to the desired degree of accuracy. A value of p is calculated for Sn which is in good agreement with some of the experiments. The large value 0.73 observed for Pb is shown to be reasonable. The values of p for the other superconducting elements are discussed. It is concluded that the observed deviations of p from $1/2$ are not necessarily in conflict with the theories of Fröhlich and Bardeen.

INTRODUCTION

THE various isotopes of a superconducting element have different transition temperatures T_c . This is the isotope effect discovered simultaneously by Maxwell of the National Bureau of Standards¹ and by Reynolds, Serin, Wright, and Nesbitt of Rutgers University.² Shortly after the discovery, the Rutgers group showed that the data of the mercury isotopes could be correlated by the formula $M^{1/2} T_c = \text{constant}$, where M is the isotopic mass.^{3,4} Since then, it has become customary to represent the data in the form⁵

$$M^p T_c = \text{constant}, \quad (1)$$

and to express the experimental results in terms of the power p . Actually, the range of M and T_c is so small that one observes more nearly the equivalent relation,

$$p = -\frac{M d T_c}{T_c d M} = -\frac{d \log T_c}{d \log M}, \quad (2)$$

arising from a plot of T_c versus M , or of $\log T_c$ versus $\log M$.

Measurements have been made of the isotope effect

¹ E. Maxwell, Phys. Rev. **78**, 477 (1950); **79**, 173 (1950).

² Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. **78**, 487 (1950).

³ Serin, Reynolds, and Nesbitt, Phys. Rev. **78**, 813 (1950); **80**, 761 (1950).

⁴ Serin, Reynolds, and Nesbitt, Phys. Rev. **84**, 691 (1951).

⁵ Herzfeld, Maxwell, Scott, Phys. Rev. **79**, 911 (1950).

for Sn, Pb, Hg, and Tl.^{4,6-11} A review of the data to the end of 1952 can be found in an article by Maxwell.¹² The results seem to indicate that p is close to $\frac{1}{2}$ for some metals, with, however, significant departures, particularly for Pb. The observed values of p are shown in Table I taken from Maxwell's review article.¹²

At the time that the data were being collected which led to the discovery of the isotope effect, Fröhlich¹³ was developing a theory of superconductivity which attributed the cause of superconductivity to the interaction of the electrons with the phonon field. The theory was developed for the temperature 0°K and led to a threshold magnetic field H_0 proportional to $M^{-1/2}$. From this, one surmises that $T_c \propto M^{-1/2}$ from the fairly well established correlation $H_0 \propto T_c$. Thus, one can take Fröhlich's theory as having predicted the isotope effect. Bardeen also proposed a similar theory at about the same time. A review of both theories has been given by Bardeen.¹⁴ Neither theory has been developed to the extent required to include significant departures from the $\frac{1}{2}$ power law.

⁶ E. Maxwell, Phys. Rev. **86**, 735 (1952).

⁷ Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. **47**, 811 (1951).

⁸ Reynolds, Serin, and Lohman, Phys. Rev. **86**, 162 (1952).

⁹ Allen, Dawton, Bär, Mendelssohn, and Olsen, Nature **166**, 1071 (1950).

¹⁰ M. Olsen, Nature **168**, 245 (1951).

¹¹ E. Maxwell and O. S. Lutes, Jr., Phys. Rev. **86**, 649 (1952).

¹² E. Maxwell, Phys. Today **5**, No. 12, 14 (1952).

¹³ H. Fröhlich, Phys. Rev. **79**, 845 (1950).

¹⁴ J. Bardeen, Revs. Modern Phys. **23**, 261 (1951).

TABLE I. The observed values of p of Eq. (2).

Element	p	Source
Sn	0.505 ± 0.019	Maxwell ^a
Sn	0.462 ± 0.014	Lock, Pippard, and Shoenberg ^b
Sn	0.46 ± 0.02	Serin, Reynolds, and Lohman ^c
Sn	0.50	Olsen, Bär, and Mendelssohn ^d
Pb	0.73 ± 0.05	Olsen ^e
Hg	0.504	Reynolds, Serin, and Nesbitt ^f
Tl	0.50 ± 0.05	Maxwell ^g

^a See reference 6.
^b See reference 7.
^c See reference 8.
^d See reference 9.
^e See reference 10.
^f See reference 4.
^g See reference 11.

In this paper, we shall develop an idea already proposed¹⁵ and show how it leads to departures of the power p from the value $\frac{1}{2}$. The discussion here is independent of the theories of Fröhlich and Bardeen, though it may be regarded as supplementing these theories. We are concerned here with the *disappearance* of superconductivity at T_c rather than with its *cause*.

THE CRITICAL TEMPERATURE

The properties of a superconductor change as the temperature rises from 0°K to T_c . In order that these properties be temperature dependent, the electrons must be sensitive to the phonon bath in which they reside. At what the observer calls a "critical temperature T_c ," we may say that the electrons find themselves in a "critical phonon field." When the phonon field is less excited than the critical state, the metal is a superconductor; when the field is more excited than the critical state, the metal is a normal conductor. This much follows rather trivially from the experimental facts and elementary notions from the theory of metals.

Now suppose that a given superconductor is at the temperature T_c and imagine that the mass of the atoms is decreased slightly without changing the temperature. Then, from lattice dynamics, the phonon field is less excited than the critical state and the metal is a superconductor. Thus, it is of secondary importance to the electrons that the temperature did not change. To return the phonon field to the critical state, while maintaining the mass at its lower value, heat must be supplied. This increases the temperature to a new T_c , higher than the original value.

The question then is how shall we relate the critical phonon field to T_c . The wavelengths, or more accurately, the propagation vectors, of lattice waves are determined by the lattice geometry and boundary conditions¹⁶ and not by the mass of the isotope. This results in the frequency ν and velocity c being proportional to $M^{-\frac{1}{2}}$ for a given propagation vector. We suspect, too, that it is the propagation vector of lattice waves

(and perhaps only the longitudinal component of these waves) which is important in interactions between electrons and lattice waves. Consequently, we shall characterize the state of the phonon field by the energy density $E(\lambda)$ at some *wavelength* λ . We do not know what wavelengths are the most important, so we suppose that it is sufficient to identify the state by the wavelength λ_m at which $E(\lambda)$ is maximum. Beginning with a given temperature T_c , a change in M shifts the peak of $E(\lambda)$. This shift may be restored by a corresponding change in T_c , and thus a generalization of Wien's displacement law applicable to real lattices will be derived. From this we can evaluate p .

THE DISPLACEMENT LAW

It is customary in lattice dynamics to employ the expression¹⁶

$$E(\nu)d\nu = \text{const} \frac{h\nu g(\nu)d\nu}{e^{h\nu/kT} - 1} \quad (3)$$

to derive the atomic heat. The energy of the modes with frequencies between ν and $\nu+d\nu$ is $E(\nu)d\nu$. The distribution of the modes is represented by $g(\nu)$. Transforming from the variable ν to the variable λ in Eq. (3), we obtain

$$E(\lambda)d\lambda = \text{const} \frac{g(c/\lambda)d\lambda}{\lambda^3(e^{hc/kT\lambda} - 1)} \quad (4)$$

Setting the derivative $dE/d\lambda$ equal to zero and using the abbreviations

$$x = h\nu/kT = hc/kT\lambda,$$

and

$$\Lambda = 3 - \frac{\lambda}{g} \frac{dg}{d\lambda} = 3 + \frac{\nu}{g} \frac{dg}{d\nu} = 3 + \frac{d \log g(\nu)}{d \log \nu}, \quad (5)$$

we find the following displacement formula:

$$e^{-x} = 1 - x/\Lambda. \quad (6)$$

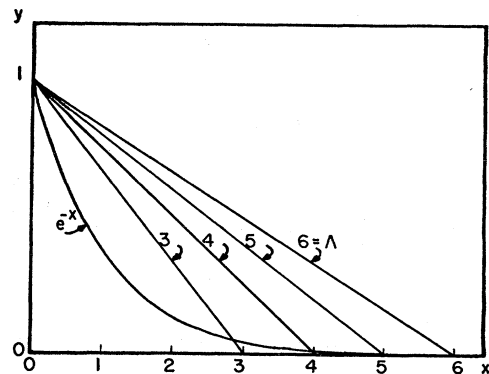


FIG. 1. The intersections of the parametric curves representing Eq. (6) yield the value of x . The straight lines are the plots of $y = 1 - (x/\Lambda)$ for the indicated value of Λ . It can be seen that for $\Lambda > 3$, a good approximation is $x = \Lambda$.

¹⁵ J. de Launay, Phys. Rev. **79**, 398 (1950).

¹⁶ See, for example, Charles Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953).

The displacement law represented by Eq. (6) is more general than that required at the low temperatures at which superconductivity usually occurs. In our domain of interest $g(\nu)$ is an increasing function of ν so that Λ is greater than 3. If we write Eq. (6) in the parametric form

$$y = e^{-x}, \quad y = 1 - x/\Lambda$$

and plot the system of curves for $\Lambda \geq 3$ shown in Fig. 1 we see that the solution of the transcendental equation is

$$x \sim \Lambda. \tag{7}$$

Formula (7) gives a value of x too large by the amount $\sim \Lambda e^{-\Lambda}$. In most cases this correction is negligible. Using Eq. (5), Eq. (7) can be written explicitly as

$$T = \frac{hc}{k\lambda_m} \Lambda^{-1} = \frac{hc}{k\lambda_m} \left(3 + \frac{d \log g}{d \log \nu} \right)^{-1}. \tag{8}$$

THE ISOTOPE LAW

Let us formulate the isotope law for the special case in which $g(\nu)$ is an increasing function of ν . From Eqs. (2) and (8) (with $T = T_c$), we obtain for p :

$$p = - \frac{M}{T} \frac{dT}{dM} = - \frac{M}{T} \frac{d}{dM} \left[\left(\frac{hc}{k\lambda_m} \right) \left(3 + \frac{d \log g}{d \log \nu} \right)^{-1} \right].$$

Since c varies as $M^{-\frac{1}{2}}$, we can differentiate c with respect to M , where it occurs explicitly, and obtain

$$p = \frac{1}{2} + M \frac{d}{dM} \log \left(3 + \frac{d \log g}{d \log \nu} \right).$$

Now we also have $\nu \propto M^{-\frac{1}{2}}$. Thus, we can transform the last expression to the more convenient form

$$p = \frac{1}{2} - \frac{\nu}{2} \frac{d}{d\nu} \log \left(3 + \frac{d \log g}{d \log \nu} \right). \tag{9}$$

An alternative form of the isotope law which we shall find useful is [see Eqs. (5) and (9)]:

$$p = \frac{1}{2} + \frac{M}{\Lambda} \frac{d\Lambda}{dM}. \tag{10}$$

LATTICE VIBRATIONS AND THE ISOTOPE LAW

Not very much is known about $g(\nu)$ for real monatomic lattices. The only adequate calculation of a lattice spectrum to which we can refer, at the present time, is that of Leighton for the face-centered cubic monatomic lattice.¹⁷ Figure 2 shows $g(\nu)$ of each of the three branches (broken curves) and the sum (continuous curve), for a special choice of the elastic constants. The general character of the curve for $g(\nu)$ does not depend, however, on these constants. We do not expect,

¹⁷ R. B. Leighton, *Revs. Modern Phys.* 20, 165 (1948).

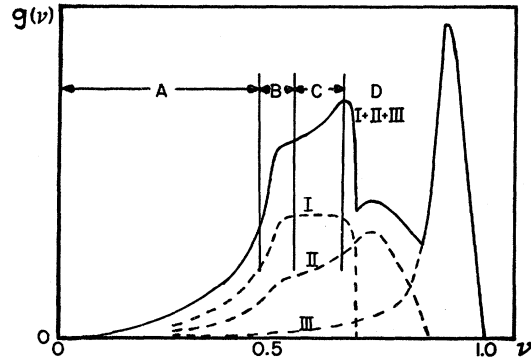


FIG. 2. A plot of $g(\nu)$ vs ν taken from Leighton (reference 17). The unit of ν here is its maximum value. The broken curves show the three branches I, II, III. The solid curve is the sum of these branches.

either, that the qualitative properties of the curve will change greatly from one crystal class to the next. So we shall assume that the qualitative aspects of $g(\nu)$ presented in Fig. 2 are typical of the metallic elements.

Figure 2 shows the spectrum divided roughly into four regions: A, B, C, D . In regions A, B , and $C, g(\nu)$ is an increasing function of ν , but in the remainder D , the function $g(\nu)$ decreases on occasion. So our comments must be limited to regions A, B , and C . Fortunately, the superconducting elements all have dominant wavelengths at T_c confined to these regions. It will help the discussion if we write $g(\nu)$ in the form

$$g(\nu) = \text{const} \nu^{N(\nu)}. \tag{11}$$

The value of $N(\nu)$ is 2 for a simple Debye spectrum. For a real lattice, $N(\nu)$ is a variable approaching the value 2 at low frequencies. From the lattice dynamics of face-centered cubic crystals the low-frequency end of $g(\nu)$ can be represented by the polynomial

$$g(\nu) = a_1 \nu^2 + a_2 \nu^4 + \dots = \sum_1^n a_n \nu^{2n}, \tag{12}$$

in which all of the coefficients are positive. This has been pointed out by Leighton.¹⁷ Comparing this with Eq. (11), we see that $N(\nu)$ begins with the value 2 near $\nu=0$, and increases steadily, approaching some value between 2 and $2n$. We have labelled this region by A . In the region B, N is decreasing, and decreases more rapidly with increasing ν than it did in region A . In region C, N does not seem to be changing very much, though it is difficult to be certain. Another of Leighton's curves (not shown in Fig. 2) shows the curve in region C concave downward instead of upward.

We shall next examine the qualitative behavior of Λ in regions A and B , and from this, estimate the behavior of p . If N is a constant, then it follows from Eq. (5) that

$$\Lambda = 3 + N. \tag{13}$$

In this case, Eq. (10) shows that $p = \frac{1}{2}$. In region A ,

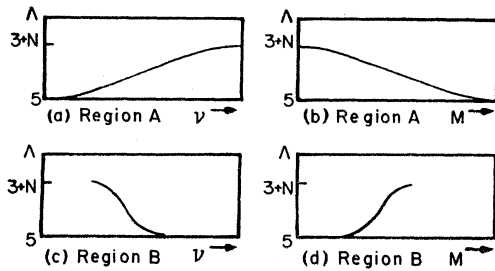


FIG. 3. The schematic behavior of Λ vs ν , and Λ vs M in regions A and B of Fig. 2. M and ν are in arbitrary units. The function Λ changes more rapidly in region B than in region A .

$N(\nu)$ changes from 2 to some value $N(>2)$. The schematic behavior of Λ as a function of ν is shown in Fig. 3(a). Figure 3(b) shows the schematic behavior of Λ as a function of $M(\nu \propto M^{-1})$. The corresponding behavior of Λ in region B is shown in Fig. 3(c), (d). The behavior of p can now be ascertained. In Fig. 3(b) we see that $d\Lambda/dM$ is negative, while in Fig. 3(d) it is positive. Consequently, from this and Eq. (10), we deduce that when the dominant wavelength falls in region A , then $p < \frac{1}{2}$; and in region B , then $p > \frac{1}{2}$. Furthermore, since $d\Lambda/dM$ can be larger in B than in A , we can expect larger deviations from $\frac{1}{2}$ in B than in A . A schematic representation of p in regions A and B is shown in Fig. 4.

So far, the discussion has been purely qualitative. This has been primarily because of the lack of any really quantitative information concerning the functions $g(\nu)$ for the various superconductors. However, in the region A , which we define as that region in which $g(\nu)$ is described by Eq. (12), we shall make a quantitative calculation of p in terms of quantities obtainable from atomic heat data. Most superconductors have their transition temperature T_c in the Debye T^3 region of atomic heat. The measured atomic heat however, does not fit a T^3 law, even after allowance has been made for the electron contribution. Regarding the Debye characteristic temperature Θ_D as a function of the temperature rather than a strict constant, one obtains from the data curves similar to the one shown in Fig. 5. Now we can calculate both p and Θ_D from the polynomial form of $g(\nu)$. The formulas so obtained enable us to compute p from the atomic heat data.

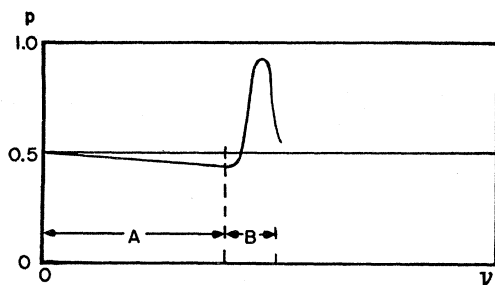


FIG. 4. The schematic behavior of p as a function of the frequency at which the peak of $E(\lambda)$ occurs.

First we compute p by substituting from Eq. (12) into Eq. (9), obtaining

$$p = \frac{1}{2} - \frac{1}{2} \nu \frac{d}{d\nu} \log \left[\sum_1^n (2n+3) b_n \nu^{2n} / \sum_1^n b_n \nu^{2n} \right], \quad (14)$$

where b_n is the ratio a_n/a_1 . If all coefficients b_n are positive, we see at once that $p < \frac{1}{2}$.

Next we compute the atomic heat by substituting for g in Eq. (3) from Eq. (12), integrating over the range $0 \leq \nu \leq \infty$, and then differentiating with respect to T . The result is

$$C_V = K \sum_1^n b_n B_{n+1} (2\pi)^{2n+2} (k/h)^{2n+2} T^{2n+1}, \quad (15)$$

where K is a constant. The b_n are identical with those in Eq. (14). B_n is the n th Bernoulli number ($B_1=1/6$, $B_2=1/30$, $B_3=1/42$, etc.). From Eq. (15), we easily

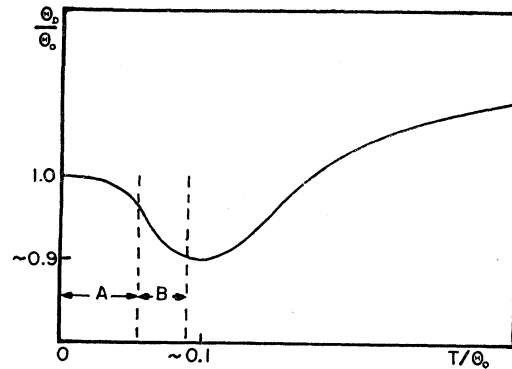


FIG. 5. A plot of Θ_D/Θ_0 vs T/Θ_0 . The regions A and B correspond qualitatively to those of Fig. 2.

obtain for Θ_D , the relation:

$$\frac{1}{\Theta_D^3} = \frac{1}{\Theta_0^3} \left[1 + \sum_2^n b_n \frac{B_{n+1}}{B_2} (2\pi)^{2n-2} (kT/h)^{2n-2} \right]. \quad (16)$$

In the derivation of Eq. (16), we disposed of such constants as K by defining Θ_0 as the value of Θ_D at $T=0^\circ\text{K}$. In principle, one determines the coefficients b_n of Eq. (16) by fitting the formula to the results of experimental work presented in the form illustrated in Fig. 5. Then p is determined by the substitution of these values of b_n into Eq. (14).

In many cases, T_c occurs at such a low temperature relative to Θ_0 that only the T^2 term in Eq. (16) need be considered in the polynomial. For these cases, Eq. (16) reduces to

$$\Theta_D = \Theta_0 \left[1 - b_2 \frac{20\pi^2}{21} \left(\frac{kT}{h} \right)^2 \right].$$

Let the symbol θ denote the fraction $(\Theta_0 - \Theta_D)/\Theta_0$. It is evident that if b_2 is positive, then θ is positive and

less than unity. We have for θ :

$$\theta = b_2 \frac{20\pi^2}{21} \left(\frac{kT}{h\nu} \right)^2. \quad (17)$$

The corresponding formula for p is

$$p = \frac{1}{2} \frac{0.4b_2\nu^2}{(1+b_2\nu^2)[1+(7/5)b_2\nu^2]}. \quad (18)$$

We now wish to express $b_2\nu^2$ occurring in Eq. (18) in terms of known quantities. Using Eq. (17), we first notice that

$$b_2\nu^2 = \frac{21}{20\pi^2} \left(\frac{h\nu}{kT} \right)^2 \theta.$$

Experimental data on atomic heat indicate that, in the range of Eq. (17), $|\theta| < 0.1$. Also the correction to $\frac{1}{2}$ in Eq. (18) is small compared to $\frac{1}{2}$. This permits us to use the approximation $(h\nu/kT) \sim 5$, the value for a Debye spectrum. Consequently, a good approximation to the value of $b_2\nu^2$ is

$$b_2\nu^2 \sim 105\theta/4\pi^2.$$

When this is substituted into Eq. (18), we finally arrive at a simple formula for p in terms of the well-defined quantity θ :

$$p = \frac{1}{2} \frac{1.06\theta}{(1+2.66\theta)(1+3.72\theta)}. \quad (19)$$

There is some reason to believe that the electrons interact principally with longitudinal waves. An isotropic crystal has a branch of purely longitudinal waves (III of Fig. 2) and two branches of purely transverse waves (I, II, of Fig. 2). A real crystal, however, is anisotropic and all three branches contain waves which are neither longitudinal nor transverse. If the average wave of branches I and II has as much as 10 percent of its amplitude parallel to the propagation vector, then these longitudinal components of the waves dominate those in branch III at low temperatures. If, in addition, the distribution of longitudinal components in branches I and II follows $g(\nu)$ in region *A*, then formula (19) will still be valid.

COMPARISON WITH EXPERIMENT

The data of Keesom and van Laer for Sn give¹⁸

$$\Theta_D = \Theta_0(1 - 0.00337^2).$$

From this we obtain $\theta = 0.0455$ and $p = 0.463$. A 10

¹⁸ W. H. Keesom and P. H. van Laer, *Physica* **5**, 193 (1938).

percent error in the coefficient of T^2 corresponds to only about 2 percent error in p . The first three data for Sn listed in Table I are the results of magnetic measurements whereas the fourth is not. The average of these three compatible data is 0.475. If we consider only the second datum, the agreement is rather good.

The $\Theta_D - T$ curve of Pb shows an inflection near 5.5°K and a minimum near 9°K. Thus T_c , which is 7.2°K, falls in region *B* of Fig. 5. This shows that Pb is likely to have a value of p greater than $\frac{1}{2}$ and that the rather large value 0.73 is entirely feasible.

The atomic heat data for mercury and thallium are not sufficiently well known to enable us to compute p . However, since $T_c/\Theta_0 \sim 0.04$ for Hg, T_c is near the inflection point near which the regions *A* and *B* join. Thus the value of p for Hg should be almost $\frac{1}{2}$, though it is difficult to ascertain whether the value is slightly greater or less than $\frac{1}{2}$. Thallium is definitely in region *A* and thus p should differ only slightly from $\frac{1}{2}$. Thus the values of p shown in Table I for these two elements are consistent with the theory.

DISCUSSION

It is possible to make an estimate of p for the remainder of the superconducting elements. Lead has the highest ratio T_c/Θ (~ 0.08). The next highest ratio is that of Hg, and probably La, being about 0.04. All other known superconducting elements have values of T_c/Θ considerably less than this, and in about half these elements, less than 0.01. On this basis, Pb is probably the only superconducting element with p significantly larger than $\frac{1}{2}$. Practically all of the elements should have $p = \frac{1}{2}$ or very slightly different from $\frac{1}{2}$. Of these elements, there exist accurate atomic heat data only for In.¹⁹ According to these data, $\theta = 0.0113$ and, therefore, $p = 0.489$.

If the treatment of the isotope effect given in this paper is correct, then the observed deviations of p from $\frac{1}{2}$ are not in conflict with the value $\frac{1}{2}$ predicted by Fröhlich inasmuch as his value was based on the theory at 0°K.²⁰

The author wishes to acknowledge here the $\Theta_D - T$ curves of various superconducting elements kindly provided by J. R. Clement, and the stimulating conversations on the subject of this paper held with both Clement and R. T. Webber.

¹⁹ J. R. Clement and E. H. Quinell, *Phys. Rev.* **92**, 258 (1953).

²⁰ It is true that the measurements on Sn by Lock *et al.* (reference 7) suggest a 0.462 power for the relation $M^2H_0 = \text{constant}$. However, one cannot overlook the fact that this value is an extrapolation to 0°K. Further, if one takes the value of 0.462 for the effect on T_c and 1/2 for that on H_0 , the value of ΔH_0 would then be 9.5 instead of 8.9 gauss. This value is not in disagreement with the data, if the data of their "virgin material" are also included.