# Effect of Temperature and of Substitutional Mo on the Magnetic Behavior of Superconducting Nb

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The temperature and mean-free-path dependence of the magnetic properties of highly reversible samples of Nb and some of its alloys with Mo are compared with recent generalizations of the Ginzburg-Landau-Abrikosov-Gor'kov theory. The temperature dependence of $\kappa_1$ and $\kappa_2$ in pure Nb is much more rapid than the theoretical predictions, as in the measurements of Finnemore *et al.* The disparity between theory and experiment decreases with increasing Mo content. The temperature dependence of the lower critical field of pure Nb is in violent disagreement with theory, while at least qualitative agreement is found in the case of the alloy samples.

## INTRODUCTION

THE Abrikosov theory[1] of the magnetic properties of an ideal type-II superconductor, applicable in the temperature range close to $T_c$, makes three definite predictions relating the shape of the magnetization curve to the Ginzburg-Landau[2] parameter $\kappa$. In the absence of surface effects, the field at which the magnetization vanishes is

$$H_{c2}=\kappa\sqrt{2}H_c, \tag{1}$$

while, for fields close to this, the magnetization follows the law

$$4\pi M=(H-H_{c2})/\beta(2\kappa^2-1), \tag{2}$$

with $\beta=1.16$ for a triangular fluxoid lattice.[3] The third prediction concerns the lower critical field $H_{c1}$; Abrikosov gives a formula valid only for a large $\kappa$, but the extension to other values has been made by Harden and Arp.[4]

Attempts[5–10] to generalize the theory to the whole range of temperatures have started from Gor'kov's[11] microscopic formulation. It is found that a single parameter $\kappa$ does not suffice to describe the three features of the magnetization curve enumerated above, and accordingly it is customary to define parameters $\kappa_1(T)$ and $\kappa_2(T)$ which replace $\kappa$ in Eqs. (1) and (2), respectively, while the temperature variation of $H_{c1}$ is usually described in terms of a third parameter $\kappa_3(T)$.

The magnitudes of $\kappa_1(T)$ and $\kappa_2(T)$ thus defined are functions of temperature and electronic mean free path. The temperature dependence of $\kappa_1$ for infinite mean free path (clean limit) has been studied by Gor'kov,[5] and for zero mean free path (dirty limit) by Maki.[6] The corresponding calculations for $\kappa_2(T)$ have been carried out by Maki and Tsuzuki[7] for the clean limit, and for the dirty limit by Maki[6] as well as by Caroli *et al.*[8]

Helfand and Werthamer[9] computed the temperature dependence of $\kappa_1$ for the intermediate values of the mean free path. Eilenberger's investigation[10] includes the effect of temperature and mean free path on $\kappa_2$ as well as on $\kappa_1$, and takes into account the possibility of $p$ as well as $s$ scattering.

The temperature dependence of the lower critical field has been[12] studied completely only in the limit of large $\kappa$, but the mean-free-path effects have been elucidated by Neumann and Tewordt[13] in the temperature region adjacent to $T_c$.

In this paper, measurements on pure Nb and on Nb alloyed with molybdenum are compared with the theoretical predictions of Eilenberger[10] (whose work includes the results of earlier investigations) and (for the temperature dependence of $H_{c1}$) those of Neumann and Tewordt.[13]

The magnetization curves of the samples studied are almost entirely reversible, so that uncertainties stemming from magnetic hysteresis are much less important than in most other work.

## EXPERIMENTAL

The niobium sample was prepared from a moderately pure rod by zone melting (several passes) followed by swaging and anneal at temperatures in excess of 2000°K for about 24 h in a vacuum better than $10^{-8}$ Torr. The resulting sample, composed of a few large crystals, exhibited a resistivity ratio of about 2000 at the time magnetization measurements were made. After aging several months at room temperature this was found to have fallen by a factor $\sim 2$.

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[5] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 833 (1959) [English transl.: Soviet Phys.—JETP **10**, 593 (1960)].
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[13] L. Neumann and L. Tewordt, Z. Physik **189**, 55 (1966).

Alloys with molybdenum were prepared by argon arc melting of the constituent metals at AERE Harwell, and subsequent zone melting at zone speeds high enough to avoid segregation. This procedure yielded almost entirely reversible material,[14] and was adopted for the preparation of all the samples used in this work.

Attempts were made to obtain even more reversible samples by annealing in the same way as for Nb, but this proved unsuccessful. Magnetization curves of samples thus treated exhibited much greater hysteresis, together with a long tail above $H_{c2}$. These effects are believed to result from the preferential evaporation of Mo during annealing, since by etching a layer of metal from the surface the original (reversible) magnetic behavior could be almost (though not quite) restored.

Magnetization measurements were made by a slightly modified version of the vibrating-sample technique reported elsewhere.[15] The sample was situated in liquid helium for measurements in the temperature range below 4.2°K, and in helium exchange gas at the higher temperatures. Temperatures greater than 4.2°K were measured by gas thermometry. The accuracy, having been checked against the susceptibility of

$$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O,$$

is estimated to be considerably better than 1%. Further details are given elsewhere.[16]

Typical magnetization curves are shown in Fig. 1. In all cases the value of $H_c$ has been computed from the mean area of the curves for increasing and decreasing fields. The magnitude of $H_c$ calculated from the area under the field *increasing* curve differed from this value by ~2% in the niobium sample, by ~3% in $Nb_{95}Mo_5$ and by <1% in all other samples.

## RESULTS

Since both theory and the present investigation suggest that the magnetic behavior depends on the size of the electronic mean free path relative to the coherence length, it is necessary to make some estimate of these quantities.

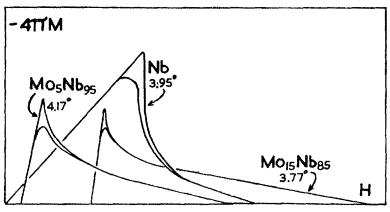


FIG. 1. Magnetization (arbitrary units) versus field for the Nb sample and for two alloy samples. Both forward and return curves are shown.

For a pure material of Ginzburg-Landau parameter $\kappa_0$ the expression[17]

$$\kappa_0 = (1.61\times10^{24} T_{c0}\gamma^{3/2}/N^{4/3})(S_f/S)^2 \quad (3)$$

enables the effective area of the Fermi surface to be computed if the electronic specific heat $\gamma$, transition temperature $T_{c0}$, and the value $S_f$ for a free-electron gas of density $N$ are known. The formula[17,18]

$$\xi_0 = 0.18kS/12\pi T_{c0}\gamma \quad (4)$$

gives the coherence length of the pure material. The present results for $\kappa_0$, and a $\gamma$ value[19] of $7.3\times10^3$ erg/cc °K yield $\xi_0 = 390$ Å. The mean free path may be calculated from[18]

$$\langle \rho_n l \rangle = 6\pi^2 h/e^2 S, \quad (5)$$

where $\rho_n$ is the residual resistivity. For the Nb studied in this work these expressions give $\xi_0/l \sim 0.025$, so that the pure limit is approached quite closely.

Accurate estimates of the mean free paths and coherence lengths for the alloys are not easily reached in the absence of detailed knowledge of the Fermi surface. Order-of-magnitude assessment of the mean free path may be made from (5) by assuming $S$ to be the same as in Nb. The coherence length may then be estimated from[20]

$$\xi = (\xi_0 l)^{1/2}, \quad (6)$$

which is applicable in the dirty limit, and may thus be considerably in error for the cleaner alloys.

Values of $\xi/l$ and $\xi_0/l$ calculated according to this prescription are set down in Table I. Also quoted is the value of $\xi/l$ estimated from the relation given by Eilenberger between this quantity and the Ginzburg-Landau parameter $\kappa$. The agreement is reasonable in view of the uncertainties inherent in the computation. We estimate $\kappa$ for the purpose of the above comparison from the extrapolation of $\kappa_1(T)$ and $\kappa_2(T)$ to $T_c$; the two values thus obtained are identical within the error of measurement, as expected from (1) and (2).

We consider first the temperature dependence of the thermodynamic critical field $H_c$, which we obtain from the mean area of the magnetization curves for increasing and decreasing fields as stated above. It is by no means certain that this procedure is better than the use of the increasing field magnetization curve, but the difference between the values of $H_c$ calculated by these two methods do not differ by more than 2%, and the difference is not markedly temperature-dependent.

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TABLE I. Details of samples. Compositions quoted are at. % (nominal). The last column gives $\xi/l$ obtained from $\kappa$ with the aid of Ref. 10. Details of the calculation of this same quantity as given in the penultimate column are to be found in the text.

| Sample | $T_c$(°K) | $\kappa(T_c)$ | $\rho_{300}/\rho_4$ | $\rho_4$($\mu\Omega$ cm) | $\xi_0/l$ | $\xi/l$ | $\xi/l$ |
|---|---|---|---|---|---|---|---|
| $Nb_{80}Mo_{20}$ | 4.24 | 3.9 | 2.69 | 7.10 | 7.3 | 2.7 | 3.7 |
| $Nb_{85}Mo_{15}$ | 5.30 | 3.6 | 3.15 | 6.05 | 6.3 | 2.5 | 3.3 |
| $Nb_{90}Mo_{10}$ | 6.38 | 3.3 | 4.10 | 4.72 | 4.9 | 2.2 | 3.0 |
| $Nb_{95}Mo_5$ | 7.84 | 2.3 | 6.69 | 3.07 | 3.2 | 1.8 | 1.7 |
| Nb | 9.20 | 0.83 | ~2000 | $\sim 2.5\times10^{-2}$ | ~0.025 | ... | ... |

Figure 2 shows the ratio of $H_c$ to its value $H_{c0}$ at $T=0$, plotted against the square of the reduced temperature. The solid line represents a "parabolic" variation of $H_c$, while the broken line is the BCS prediction. The temperature variation of the critical field of pure Nb is closer to the parabolic law than to the BCS law. Finnemore *et al.*[21] have noticed this behavior and attribute it to a moderately strong coupling.

In spite of the rather large scatter of the experimental points a distinct tendency for the temperature variation to change, with increasing Mo content, from parabolic to BCS is discernable in Fig. 2. This suggests that the coupling becomes weaker as the Mo content is increased, as is reasonable in view of the strong fall in $T_c$ with increasing Mo content (Table I).

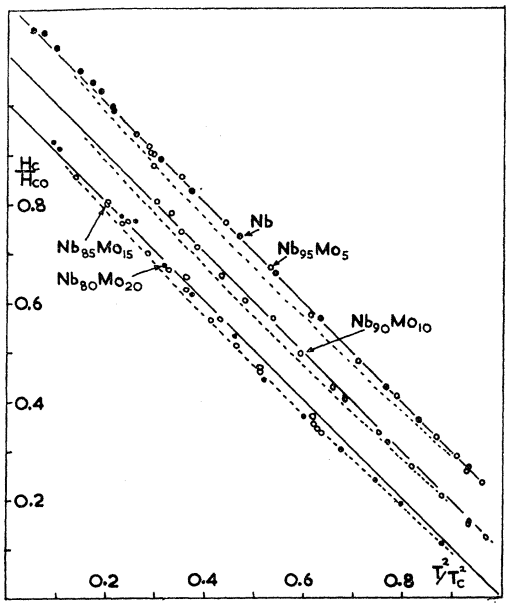


FIG. 2. Thermodynamic critical field as a function of temperature. Solid line represents a parabolic variation and the dotted line the BCS prediction. For clarity the experimental points for some samples have been displaced upwards and the theoretical curves redrawn.

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It is customary to analyze the temperature dependence of $H_{c2}$ in terms of the parameter $\kappa_1$ defined by $\kappa_1=H_{c2}/H_c\sqrt{2}$. The relevant theories, however, proceed by calculating $H_{c2}$ and dividing by the BCS value of $H_c$ to give

$$\kappa_1'=H_{c2}/\sqrt{2}H_c(\mathrm{BCS}).$$

Since we wish to compare our observed values of $H_{c2}$ to those predicted, it is convenient to work in terms of $\kappa_1'$ rather than $\kappa_1$. For the dirtiest alloys the temperature variation of $H_c$ is essentially that predicted by BCS so that $\kappa_1'\approx\kappa_1$, but for pure Nb and the cleaner alloys the temperature variation of $H_c$ differs from the BCS prediction so that $\kappa_1'<\kappa_1$.

Figure 3 shows the temperature variation of $\kappa_1'$ in the five samples studied. The parameter $\kappa'$ is defined as the limiting value of $\kappa_1'$ for $T\to T_c$. For each sample, the theoretical[10] temperature dependence of $\kappa_1'$ is shown for the clean limit (upper curve) and for the dirty limit (lower curve). In the samples of shortest electronic mean free path ($Nb_{85}Mo_{15}$ and $Nb_{80}Mo_{20}$) the temperature dependence of $\kappa_1'$ is in accordance with theory within the limit of experimental error. As the electronic mean free path is reduced the temperature dependence of $\kappa_1'$ becomes stronger. This increase is qualitatively in accord with theory,[10] but its magnitude is considerably greater than expected. Thus, the temperature variation in $Nb_{90}Mo_{10}$ is already in excess of the prediction for the clean limit, and the ratio $\kappa_1'(0)/\kappa_1(T_c)$ for pure Nb is well in excess of the pure-limit prediction, as noted by Finnemore *et al.*[21]

A discrepancy between theory and experiment in the pure limit also occurs in the case of the parameter $\kappa_2$ (Fig. 4). Again, the observed temperature variation is considerably stronger than the theoretical estimate.

For the alloys, comparison of $\kappa_2$ with theory requires knowledge of the ratio of $s$ to $p$ scattering. The theoretical curves in Fig. 5 are drawn for the case of pure $s$ scattering, with values of $\xi/l$ equal to 2 (upper curve) and 6 (lower curve), marking the approximate range appropriate to these alloys (Table I). For the dirtier alloys, the temperature dependence of $\kappa_2$ is in reasonable agreement with

theory. As the mean free path is reduced the temperature variation of $\kappa_2$ becomes stronger than the theoretical prediction. This disparity would be even greater were a more reasonable ratio of $p$ to $s$ scattering assumed.

Thus the behavior of the parameter $\kappa_2$ is rather similar to that of $\kappa_1'$ in that there is fairly good agreement with theory for the dirtier samples, and a progressive departure from theory with increasing elec-

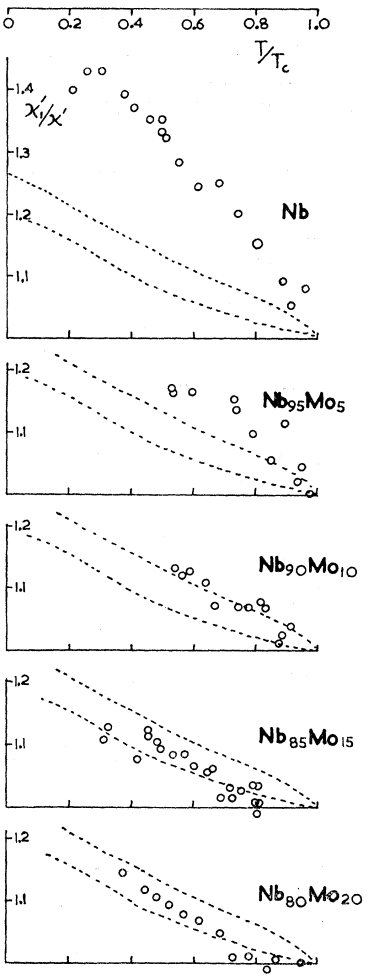


FIG. 3. The ratio $\kappa_1'/\kappa$ as a function of reduced temperature. The broken curves represent the theoretical prediction (Ref. 10) for the clean limit (upper curve) and the dirty limit (lower curve).

tronic mean free path until, in the pure limit, the variation of both $\kappa_2$ and $\kappa_1'$ is much stronger than expected.

Measured values of $H_{c1}$ will be compared with the calculations of Neumann and Tewordt,[13] which are valid for all values of $H_{c1}/H_c$, although only in the region $T \approx T_c$ (the calculation by Maki[12] is valid for all $T$, but its validity is confined to the limit of large $\kappa$ and it is inapplicable to our samples).

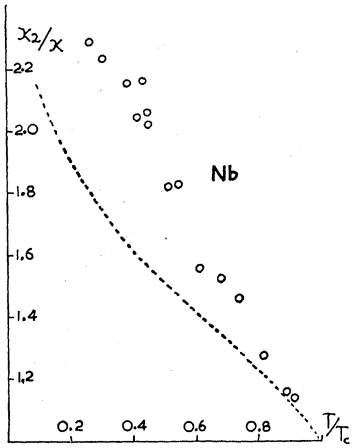


FIG. 4. The ratio $\kappa_2/\kappa$ for the Nb sample as a function of reduced temperature. The broken curve is the theoretical prediction (Ref. 10) for the clean limit.

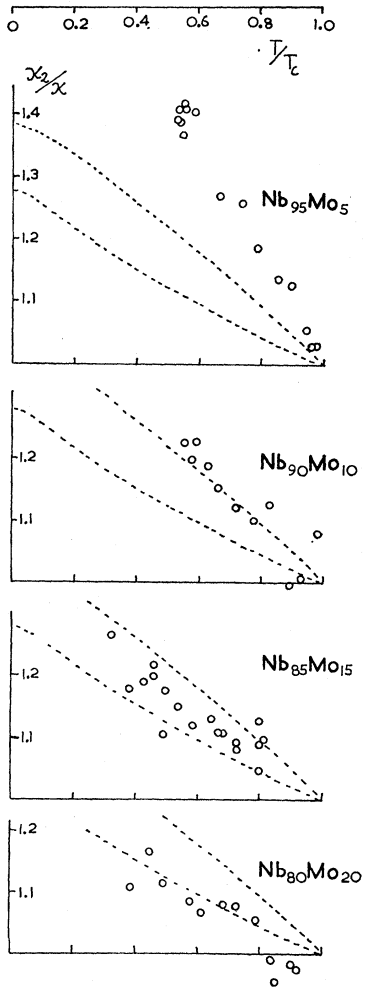


FIG. 5. The ratio $\kappa_2/\kappa$ for the alloy samples. Theoretical (Ref. 10) curves are drawn for $\xi/l=2$ (upper curve) and 6 (lower curve) for the case of pure $s$ scattering.

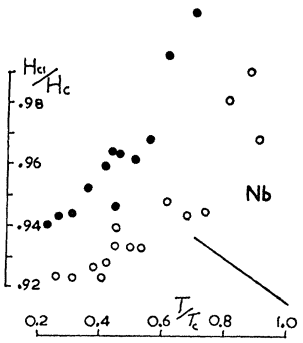


FIG. 6. The ratio $H_{c1}/H_c$ for the Nb samples. Open circles are for the observed $H_c$ and closed circles for the BCS $H_c$. The line represents the theoretical prediction of Ref. 13.

Open circles in Fig. 6 show the observed ratio $H_{c1}/H_c$ as a function of $T/T_c$. $H_c$ is obtained from the magnetization curve as described above. For comparison we show also values of $H_{c1}/H_c$ (BCS) (closed circles). The difference between these two sets of points emphasizes the disparity between the experimental value of $H_c$ and the BCS value (Fig. 2). The short line is the theoretical estimate[13] of $H_{c1}/H_c$, valid for $T \approx T_c$. Agreement as to the magnitude of $H_{c1}/H_c$ is reasonably good, but the predicted temperature dependence differs even in sign from that observed.

Values of $H_{c1}/H_c$ for the alloy samples are plotted as a function of $T/T_c$ in Fig. 7. The short lines are the theoretical curves ($T \approx T_c$) for 0.88 $\xi_0/l$ equal to 2 (upper line) and 10 (lower line), which covers the approximate range of $\xi_0/l$ in these alloys (Table I). Agreement of the observed and predicted magnitudes of $H_{c1}$ is good in all cases. The scatter of the experimental data and its scarcity in the relevant temperature region precludes any detailed comparison with the theoretical temperature dependence of $H_{c1}/H_c$, but we can at least conclude that the theory is not qualitatively in error, as is the case for the pure sample. There seems to be a tendency for $H_{c1}/H_c$ to decrease rather more rapidly with temperature than the calculations suggest, but firm conclusions must await more accurate measurements in the region near to $T_c$.

## DISCUSSION

The temperature variation of $\kappa_1'$ and $\kappa_2$ exhibits a systematic dependence on impurity content. Samples of short electronic mean free path behave in a manner more or less consistent with theory, but the experimental observations show an increasing departure from theory as the mean free path increases, and the disparity becomes quite pronounced in the limit of long mean free path.

The addition of Mo to Nb introduces factors other than the straightforward change in mean free path considered in the theory.[10] Figure 2 suggests that one such factor is a change in the coupling strength. This is interesting in view of the suggestion[22] that the temperature dependence of $\kappa_1'$, at least, may be influenced by coupling strength. On the other hand, recent theoretical considerations[23] indicate that this factor is not likely to be of sufficient importance to account for anomalies of the magnitude observed here.

It is more likely that the observed deviations are related to anisotropy associated with the nonspherical Fermi surface.[24] The tendency for the temperature dependence of $\kappa_1'$ and $\kappa_2$ to become rapidly weaker with increasing Mo content is compatible with the expected fall in anisotropy effects with decreasing electronic mean free path.

Fietz and Webb[25] have recently reported an inves-

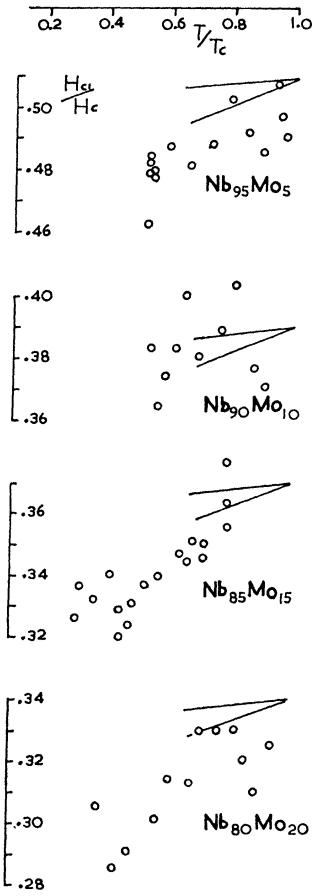


FIG. 7. Temperature dependence of $H_{c1}/H_c$ for the alloy samples. The theoretical prediction (Ref. 13) for $T \approx T_c$ is indicated by lines drawn for $0.88\xi_0/l = 2$ (upper curve) and 10 (lower curve).

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tigation similar to ours, with Ti rather than Mo as the solvent. Their conclusions are similar to ours, except that they find an anomalously strong variation of $\kappa_1'$ and $\kappa_2$ for all values of $\xi/l$, whereas in the present work the temperature dependence of $\kappa_1'$ and $\kappa_2$ is compatible with the theory, within the experimental error, for the samples of shortest mean free path.

The theory of Neumann and Tewordt[13] accounts very well for the magnitude of $H_{c1}/H_c$ in all samples. Their estimate of the temperature dependence of this quantity is in violent disagreement with our observations on pure Nb. In the case of the alloy samples, their calculation is at least in qualitative agreement with the data. There is some indication that the theory underestimates the rate of change with temperature, but the accuracy of measurement does not warrant definite conclusion.

One would, perhaps, expect to find systematic errors in $H_{c1}$ due to surface effects.[26] The fact that theory[13] gives a good account of the observed magnitude of $H_{c1}$, and the almost complete absence of hysteresis in the alloy samples, suggests that this is not so. The reason why surface effects are absent is not clear; it is presumably related to some special surface condition in these samples.

## ACKNOWLEDGMENTS

We are obliged to P. E. Madsen, C. H. Thomas, and G. Taylor for assistance in preparing the specimens, and to K. Mendelssohn for his critical interest. Financial support was provided by the Ministry of Technology.

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# Ultrasonic Attenuation in Superconducting Mercury and Mercury-Cadmium Single Crystals*†

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This paper presents the results of low-temperature ultrasonic-attenuation studies in mercury single crystals, polycrystals, and mercury single crystals with varying concentrations of cadmium impurity. The frequency ranged from 10 to 130 MHz and the doping concentration from 0.01 to 0.10% by weight. The major emphasis is a systematic study of the deviations of $\alpha_s/\alpha_n$ for longitudinal ultrasound from that predicted by the BCS theory. These deviations are a drop in $\alpha_s/\alpha_n$ with decreasing temperature near $T_c$ which is greater than that predicted by BCS. The rapidity of the drop increased with increasing frequency in all pure samples, was frequency-independent, and decreased with doping concentration in the doped samples. The deviations observed cannot be explained adequately by dislocation attenuation or by multiple anisotropic energy gaps.

## I. INTRODUCTION

DURING the past several years there has been a growing interest in the significant deviations from theoretically predicted values displayed by the attenuation of longitudinal ultrasound in superconductors. Bardeen, Cooper, and Schrieffer (BCS),[1] Tsuneto,[2] and others calculate that the ratio of the electronic attenuation in the superconducting state to that in the normal state should be

$$\alpha_s/\alpha_n = 2\{1+\exp[\Delta(T)/kT]\}^{-1}, \quad (1)$$

where $\Delta(T)$ is the superconducting energy gap. Measurements of this ratio in pure superconductors seldom follow Eq. (1), the deviation usually appearing near $T_c$ as a too rapid decrease of $\alpha_s/\alpha_n$ with decreasing temperature. The most extreme example of this effect yet reported is by Deaton,[3] who worked with a very pure unstrained lead crystal, but other workers have observed the too rapid drop in other materials: polycrystalline mercury,[4] single-crystal mercury,[5] single-crystal tin,[6–8] single-crystal lead and lead doped with

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