

## Ultrasonic Absorption by Superconducting Nb-Zr Alloys

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Ultrasonic attenuation studies in dilute superconducting Nb-Zr alloys have revealed strongly temperature-dependent absorption peaks which cannot be explained in terms of single electron-phonon scattering processes. The set of temperatures at which these peaks occur is dependent on the frequency of the sound wave and the strain content of the sample. A phenomenological model is proposed which interprets the absorption peaks as being due to an exchange of energy which occurs when the sound frequency is equal to one of a set of collective excitation modes of the electron gas. The assumptions on which the model is based are the same as those which yield collective excitations within the energy gap in more fundamental descriptions of the superconducting state. The phenomenological treatment involves a hydrodynamic approach in a finite superconducting phase, based on volume derivatives of the electronic free energy under conditions of charge neutrality. The interaction constant for the collective excitations is empirically assumed to be decreased by the factor,  $\chi(r_0) \equiv \xi^{-1} r_0 \exp(\alpha - \xi r_0^{-1})$ , when the extent of the superconducting phase  $r_0$  is less than the coherence distance  $\xi$ . Good agreement between the experimental data and the results of the proposed model is obtained.

### INTRODUCTION

THE study of the attenuation of ultrasonic waves by pure metals at low temperatures has yielded considerable insight into the interaction between phonons and the conduction electrons in both normal and superconducting metals. Morse<sup>1</sup> has discussed this interaction in detail. Concisely, the magnetoacoustic effect has been fruitful in the mapping of Fermi surfaces, and attenuation measurements made below the critical temperature in elemental superconductors have provided a striking verification of the Bardeen-Cooper-Schrieffer<sup>2</sup> (BCS) theory of superconductivity. In view of the short electron mean free path in alloys and in impure elemental solids, it has long been felt that there would be no observable electronic contribution to the ultrasonic attenuation. In this paper, recent measurements of the attenuation of ultrasonic waves in samples of Nb-Zr alloys are reported; this paper reports an extension of previously discussed experiments by the authors<sup>3</sup> and contains details of a phenomenological calculation based upon the model of hard superconductivity which incorporates a filamentary structure. The model is successful in predicting some quantitative features of the structure in plots of attenuation versus temperature, in the superconducting state. Results of measurements on the influence of heat treatment on the behavior of the attenuation with temperature are reported and are discussed in terms of the proposed model.

### EXPERIMENTS

The superconducting alloys were prepared by arc melting in an inert atmosphere previously weighed samples of niobium and zirconium bar stock. X-ray and

emission spectroscopy indicated that the samples were uniform solid solutions and contained no zirconium in a precipitated phase. The samples, after being lapped to yield two parallel faces, are roughly described as cylinders of 1¼-in. diam and ¾-in. length. The ultrasonic attenuation measurements were made by the pulse-echo technique with equipment of the type described by Chick *et al.*<sup>4</sup>; on occasion, the pulse-echo equipment described by Einspruch and Manning<sup>5</sup> was used. A radio frequency pulsed oscillator is used to excite a quartz transducer which is bonded to the sample by a thin layer of Nonaq<sup>6</sup> stopcock grease. The mechanical pulse, produced by the transducer, is reflected each time it reaches the face of the sample opposite to the transducer; after each transit, some of the mechanical energy is sampled and reconverted to electrical energy by the same transducer. These electrical signals are amplified, detected, and displayed on an oscilloscope. The variation with temperature of echo height is monitored with a calibrated pulse comparator; the temperature dependence of the change in the attenuation is thus obtained.

### EXPERIMENTAL RESULTS

The initial observations made in an unannealed Nb-1% Zr alloy were reported previously<sup>3</sup> and are shown in Fig. 1. The following conclusions were reached in regard to the mechanism producing the resonance peaks: (1) It is a property of the superconducting state. (2) It is probably related to pressure and/or charge density modulations. (3) The set of temperatures at which peaks occur is strongly dependent on the frequency of the sound wave. (4) The amplitude of the peaks decreases as the frequency of the sound wave increases. (5) The mechanism is not dependent on the

<sup>1</sup> R. W. Morse, *Progress in Cryogenics*, edited by K. Mendelssohn (Academic Press Inc., New York, 1959), Vol. 1, p. 221.

<sup>2</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

<sup>3</sup> L. T. Claiborne and N. G. Einspruch, *Phys. Rev. Letters* **10**, 49 (1963).

<sup>4</sup> B. B. Chick, G. P. Anderson, and R. Truell, *J. Acoust. Soc. Am.* **32**, 186 (1960).

<sup>5</sup> N. G. Einspruch and R. J. Manning, *J. Acoust. Soc. Am.* **35**, 215 (1963).

<sup>6</sup> Nonaq, Fisher Scientific Company.

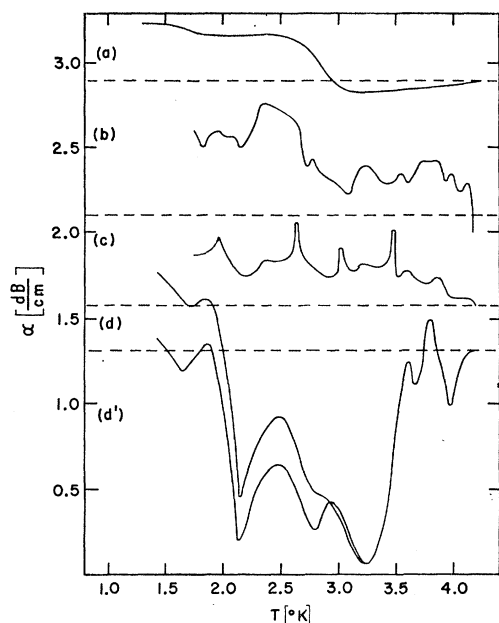


FIG. 1. (a) Relative attenuation ( $\text{dB cm}^{-1}$ ) at  $10.0 \text{ Mc sec}^{-1}$  as function of temperature for 99.9% pure Nb. (b), (c), (d) Attenuation ( $\text{dB cm}^{-1}$ ) as function of temperature in Nb-1.0% Zr alloy for 29.0, 16.5, and  $10.0 \text{ Mc sec}^{-1}$ , respectively. (d') Data of curve (d) with background (a) removed.

amplitude of the sound wave for the small strains used in this experiment.

Measurements of the temperature dependence of the compressional wave absorption in other Nb-Zr alloys have been made over the same range of frequency ( $5$  to  $30 \text{ Mc sec}^{-1}$ ) and temperature ( $1.3$  to  $4.2^\circ\text{K}$ ). Structure similar to that in Fig. 1 was found for all samples tested (1.0%, 2.1%, 2.6%, 3.6%, and 4.5% Zr). The most meaningful comparison of results is made for annealed samples, since the dislocation structure resulting from preparation can vary greatly from sample to sample. Figure 2 shows the temperature variation of the absorption at  $12 \text{ Mc sec}^{-1}$ . From Figs. 2(a) and 2(b), one can see that some of the peaks are reduced in amplitude as the sample is annealed, while the temperature at which each peak occurs is essentially unchanged. One can also see that the structure which remains after 16 h of annealing is the same for the 1.0% Zr and the 2.6% Zr samples, except for a possible small difference in amplitudes. In the absence of a model to explain these results, a reasonable inference might be that the peaks which are removed by annealing are related to dislocations, and the remaining peaks are due to the presence of the Zr ions. These results will be discussed later in terms of a model proposed in the next section.

#### PHENOMENOLOGICAL THEORY

A phenomenological treatment of the attenuation of compressional sound waves in metals via single, conduction electron-lattice scattering can be made from a consideration of electron ion density modulations under

conditions of charge neutrality (cf. Pippard<sup>7</sup>). Starting with the Boltzmann transport equation and invoking Maxwell's equations, one can derive an expression for conversion of energy from the sound wave to random thermal energy due to irreversible scattering of the electrons. The electron and lattice systems are separated except for the fact that the electron distribution must follow the lattice ions in order to cancel the electric fields arising from displacements of the ions. The energy loss mechanism for the electron-lattice system is the random scattering of the electrons by impurities or thermal phonons. The expression derived by this approach should be valid for all sound frequencies up to the Debye cutoff frequency for the particular lattice. In general, this electronic attenuation is a monotonically increasing function of the parameter  $ql_e$  where  $q$  is the magnitude of the propagation vector of the compressional wave and  $l_e$  is the electron mean free path.

When  $ql_e$  becomes an order of magnitude less than unity, the electronic attenuation becomes negligible. Therefore, for sound frequencies of  $10^7$  to  $10^8$  cps,  $l_e$  must be of the order of  $10^{-2}$  to  $10^{-3}$  cm in order for the electronic attenuation to be measurable. This condition can be achieved only for extremely pure metals ( $\sim 99.999\%$ ) at liquid-helium temperatures. It can be seen that for superconducting alloys, which have high-strain content as well as high-impurity content, the ultrasonic attenuation due to single-electron processes should be quite small. The data cited in the last section, however, indicate that there is some mechanism for temperature- and frequency-dependent compressional wave ultrasonic absorption which is characteristic of the superconducting state. Since the temperature dependence of the parameters of the superconducting state is determined by the electronic properties, it follows that there must be some additional mechanism for interaction between the lattice vibrations and the electron distribution which has been overlooked heretofore.

Anderson<sup>8</sup> and Bogoliubov<sup>9</sup> have shown that there

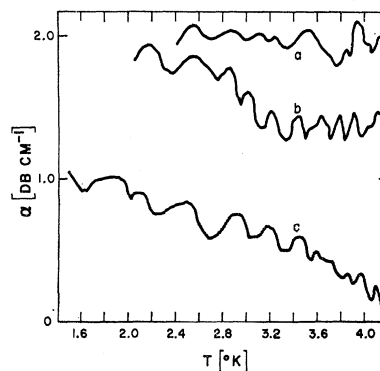


FIG. 2. Relative attenuation ( $\text{dB cm}^{-1}$ ) at  $12.0 \text{ Mc sec}^{-1}$  as a function of temperature for (a) Nb-1.0% Zr after 2-h anneal; (b) Nb-1.0% Zr after 18-h anneal; and (c) Nb-2.6% Zr after 16-h anneal.

<sup>7</sup> A. B. Pippard, *Phil. Mag.* **46**, 1104 (1955).

<sup>8</sup> P. W. Anderson, *Phys. Rev.* **112**, 1900 (1958).

<sup>9</sup> N. N. Bogoliubov, *Zh. Eksperim. i Teor. Fiz.* **34**, 58 (1957) [translation: *Soviet Phys.—JETP* **7**, 41 (1957)].

are low-frequency, collective-type excitation modes for the electrons in the superconducting state which correspond to pressure waves in a neutral Fermi gas. The basic equation used in the hydrodynamic formalism for plasma oscillations involves terms in the electromagnetic fields and a term in the pressure gradient. Pressure gradient effects for normal metals are negligible compared to the electric field effects; however, pressure effects in superconductors become dominant for low-frequency density modulations. Such modes would decay rapidly in the normal state, for which the density of states is finite at the Fermi surface, while excitation states lying within the superconducting energy gap have long lifetimes. The excitations have been shown to enter into both real and virtual processes. The high-frequency plasmon modes, for which Coulomb forces are important, exist in the superconducting state and are essentially unchanged from the normal state.

The authors' initial paper<sup>3</sup> on the subject of the ultrasonic absorption peaks included an analysis based on isothermal displacements of a phase boundary between two types of superconducting material. An equilibrium position of the phase boundary, under the constraints of the system, which minimized the electronic free energy was assumed. Displacement of the boundary would lead to a linear restoring pressure, hence, to a set of temperature-dependent resonant modes of vibration for the phase boundary. A major difficulty arises, however, when one attempts to assign an inertia to the boundary. In the initial paper an inertial density of the order of the electron-mass density was assumed. The form of the resonance condition, obtained by setting the sound frequency equal to one of the harmonic frequencies of vibration for the phase boundary, was in good agreement with the Nb-Zr absorption data, and permitted a simple interpretation of the absorption peaks. It will be shown below that a consideration of density modulations within the electron gas in a finite single phase under conditions of charge neutrality leads to the same form for the resonance condition without the difficulty in determining the inertial density. It is now recognized that the present analysis is simply a phenomenological derivation of the excitation modes, with appropriate boundary conditions, for a superconducting phase of finite dimensions. The special case for which the phase boundary is free to move with the electron density variations was considered in the initial paper. Here, a more general phenomenological approach will be considered in so far as density modulations within a single phase will be considered, and the resonance conditions will be obtained for both fixed and free phase boundaries.

The derivation will proceed from a hydrodynamic approach. For the low-frequency collective excitations in the superconducting state, the electric field effects are neglected. Specifically, it will be assumed that for sufficiently slow local variations of electron density with respect to a fixed lattice, the long-range Coulomb inter-

actions can be neglected so that the important restoring forces on the electron distribution arise from the pressure gradients. Then, the pressure-density relation for the electron plasma can be obtained from the isothermal volume derivative of the Helmholtz free energy. It will be shown that the isothermal condition does indeed, apply to density modulations in the frequency range to be considered.

The concept of a pressure associated with the superconducting state was first considered in regard to the electromagnetic stresses at the boundary of a superconducting region. A change in volume  $\delta V$  of the superconducting phase, which involves no change in free-energy density  $f$  changes the total internal free energy  $F$  by an amount

$$\delta F = -(f_n - f_s)\delta V. \quad (1)$$

Normal material is converted to superconducting material in  $\delta V$ . There is an effective pressure  $P = -\delta F/\delta V$  which does work against the electromagnetic stresses, and in equilibrium

$$(f_n - f_s) = \frac{1}{2}\Lambda j_{s11}^2 \approx -\frac{1}{8\pi}H_c^2(T), \quad \Lambda = \frac{4\pi\lambda^2}{c^2}, \quad (2)$$

where  $\lambda$  is the penetration depth,  $j_{s11}$  is the surface current, and  $H_c(T)$  is the critical field.<sup>10</sup> This difference in energy density is defined to be the Meissner pressure. In order to find the electron gas pressure in the superconducting state, a volume change which implies a change in electron density must be considered. It should be mentioned that in the superconducting state there is an ambiguity between the Helmholtz and Gibbs free energy. Thus, an isothermal volume derivative of the BCS free energy has the form of a true pressure. The superconducting, electronic free energy in volume  $V$  is

$$F_s = -\frac{1}{2}V[n_F\epsilon^2(T) - S_s(T)], \quad (3)$$

where  $n_F$  is the density of states at the Fermi level,  $\epsilon(T)$  is the temperature-dependent energy gap, and  $S_s$  is the entropy of the superconducting state.

### Single-Phase Superconductors

Consider a single phase of superconducting material occupying  $V$ . Since there is only a change in the electronic free energy between the normal and superconducting state to a first approximation,

$$F_s = F_n - (1/8\pi)H_c^2(T). \quad (4)$$

The actual temperature dependence of  $H_c(T)$  and  $F_s$  is complicated; however, the Gorter-Casimir<sup>11</sup> relation

$$H_c(T) = H_c(0)[1 - (T/T_c)^2] \quad (5)$$

is within about 4% of the BCS prediction and is as-

<sup>10</sup> F. London, *Superfluids* (Dover Publications Inc., New York, 1960), Vol. 1, p. 138.

<sup>11</sup> C. J. Gorter and H. B. G. Casimir, *Physik. Z.* **35**, 963 (1934).

sumed to be correct. For simplicity, Eq. (4) will be used for the isothermal derivative of the free energy with respect to volume. The variation of  $H_c(0)$  and  $T_c$  with respect to volume can be found from the variation of  $\epsilon(0)$  and  $n_F$  according to the simple BCS relations

$$\begin{aligned} H_c(0) &= [4\pi n_F]^{1/2} \epsilon(0), \\ T_c &= z\epsilon(0), \end{aligned} \quad (6)$$

where  $z$  is a constant. In a semiempirical calculation of the transition temperature and the effects of pressure on the transition, including the contribution of *umklapp* processes to the electron-phonon interaction, Morel<sup>12</sup> developed a formalism for the variation of  $\epsilon(0)$  with volume changes, i.e.,

$$\begin{aligned} \frac{d \ln \epsilon(0)}{d \ln r_s} &= -3\gamma + \ln \left( \frac{0.85 \Theta_D}{T_c} \right) \left[ \frac{d \ln n_F}{d \ln r_s} + 2 \right] \\ &+ \ln^2 \left( \frac{0.85 \Theta_D}{T_c} \right) \left[ \frac{m^*}{m} \frac{a^2}{2(1+a^2)} \right], \end{aligned} \quad (7)$$

where  $r_s$  is the Fermi-Thomas radius,  $\gamma$  is the Grüneisen constant,  $\Theta_D$  is the Debye temperature,  $m$  is the electron mass,  $m^*$  is the normal electronic effective mass, and  $a^2 = 0.167 r_s$ .  $r_s$  is defined by  $\frac{4}{3}\pi(a_0 r_s)^3 = 1/N$ , where  $a_0$  is the Bohr radius and  $N$  is the number of electrons per unit volume. If a small linear displacement  $y$  of one surface of area  $\mathcal{A}$  of the volume element is considered, and if the second derivative of  $\epsilon(0)$  with respect to  $r_s$  exists and is positive, then it will be shown that there exists an excess pressure linear in displacement which will lead to a hydrodynamic wave equation.

Let  $V(y) = \mathcal{A}[l-y]$ . The total hydrodynamic pressure of the neutral Fermi gas is

$$P_s = -(\partial F_s / \partial V)_T = \mathcal{A}^{-1} \left( \frac{\partial F_s}{\partial y} \right)_T. \quad (8)$$

From Eq. (4) it follows that

$$\begin{aligned} P_s &= -\frac{1}{3}\pi^2(k_B T)^2 l \left( \frac{\partial n_F}{\partial y} \right)_T - 2 \frac{H_c(T)}{8\pi} l \left( \frac{\partial H_c(T)}{\partial y} \right)_T \\ &+ \left[ \frac{1}{3}\pi^2(k_B T)^2 n_F + \frac{1}{8\pi} H_c^2(T) \right], \end{aligned} \quad (9)$$

where  $F_n$  is defined by  $F_n = -\frac{1}{3}\pi^2(k_B T)^2 n_F$ ; and  $k_B$  is the Boltzmann constant. The partial derivatives of  $\epsilon(0)$ ,  $n_F$ , and  $T_c$  with respect to  $y$  will have the forms

$$\begin{aligned} \frac{\partial \epsilon(0)}{\partial y} &= \frac{\epsilon(0)}{l} \left( P + Q \frac{y}{l} \right), \\ \frac{\partial T_c}{\partial y} &= \frac{T_c}{l} \left( P + Q \frac{y}{l} \right), \\ \frac{\partial n_F}{\partial y} &= \frac{n_F}{l} \left( A + B \frac{y}{l} \right). \end{aligned} \quad (10)$$

The constants  $P$ ,  $Q$ ,  $A$ , and  $B$  will be determined below. Since

$$\begin{aligned} \left( \frac{\partial H_c(T)}{\partial y} \right)_T &= \frac{\partial H_c(0)}{\partial y} \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right] \\ &+ H_c(0) \frac{\partial}{\partial y} \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right], \end{aligned}$$

then

$$\begin{aligned} \left( \frac{\partial H_c(T)}{\partial y} \right)_T &= \frac{H_c(0)}{2l} \left\{ \left[ (A+2P) + (B+2Q) \frac{y}{l} \right] \right. \\ &\left. - \left( \frac{T}{T_c} \right)^2 \left[ (2P-A) + (2Q-B) \frac{y}{l} \right] \right\}. \end{aligned} \quad (11)$$

When coefficients of powers of  $(y/l)$  are collected, the complete hydrodynamic pressure is

$$\begin{aligned} P_s &= \frac{H_c^2(0)}{8\pi} \left\{ \left[ 1 - (A+2P) \right] + \left[ (4P-2) + \beta(1-A) \right] \right. \\ &\quad \left. \times \left( \frac{T}{T_c} \right)^2 + \left[ 1 - (2P-A) \right] \left( \frac{T}{T_c} \right)^4 \right\} \\ &+ \frac{H_c^2(0)}{8\pi} \left( \frac{y}{l} \right) \left\{ - (B+2Q) + (4Q-\beta B) \left( \frac{T}{T_c} \right)^2 \right. \\ &\quad \left. - (2Q-B) \left( \frac{T}{T_c} \right)^4 \right\}, \end{aligned} \quad (12)$$

where  $\beta = -\frac{1}{3}\pi^2 n_F (k_B T_c)^2 [H_c^2(0)/8\pi]^{-1}$ . According to BCS theory, the constant  $\beta$  is a universal constant ( $\beta = 2.14$ ) which expresses the law of corresponding states for superconductors. For real superconductors, the simple relation  $\epsilon(0) = 1.75 T_c$  does not always hold; therefore,  $\beta = (2.14)(1.75/z)^2$ , where  $z$  is defined by Eq. (6). The first term in Eq. (12) represents the hydrostatic pressure  $P_0$ ; the second term represents the excess pressure,  $P_e$ , which is linear in the displacement  $y$ . The total electron density is  $\rho = \rho_0(1+y/l)$ ; the excess density corresponding to  $P_e$  is  $\rho_e = \rho_0(y/l)$ , where  $\rho_0$  is the unperturbed electron density. Extrapolating to a continuum representation of the electron gas, one expects a velocity of propagation for a compressional wave to be

$$\begin{aligned} c^2 = P_e \rho_e^{-1} &= \frac{H_c^2(0)}{8\pi \rho_0} \left\{ - (B+2Q) + (4Q-\beta B) \left( \frac{T}{T_c} \right)^2 \right. \\ &\quad \left. - (2Q-B) \left( \frac{T}{T_c} \right)^4 \right\}. \end{aligned} \quad (13)$$

It remains to be shown from an evaluation of the constants that  $c$  is real.

The assumption will be made that the second deriva-

<sup>12</sup> P. Morel, J. Phys. Chem. Solids **10**, 277 (1959).

tive of  $\epsilon(0)$  with respect to volume changes can be obtained from Eq. (7). For an isotropic medium,

$$l \frac{d \ln \psi}{dy} = -\frac{1}{3} \frac{d \ln \psi}{d \ln r_s}, \quad (14)$$

where  $\psi$  is any continuous function of volume. Thus, the constants will be found from derivatives with respect to  $r_s$ . Hence,

$$\begin{aligned} \frac{\partial^2 \epsilon(0)}{\partial r_s^2} = & \left[ \frac{1}{r_s} \frac{\partial T_c}{\partial r_s} - \frac{T_c}{r_s^2} \right] \left[ \frac{\partial \ln \epsilon(0)}{\partial \ln r_s} \right] \\ & + \left[ \frac{T_c}{r_s} \right] \left\{ \frac{\partial}{\partial r_s} \ln [0.85 \Theta_D T_c^{-1}] \left( \frac{\partial \ln n_F}{\partial \ln r_s} + 2 \right) \right. \\ & + \frac{\partial}{\partial r_s} \ln^2 [0.85 \Theta_D T_c^{-1}] \left( \frac{m^*}{m} \frac{a^2}{2(1+a^2)} \right) \\ & + \ln^2 [0.85 \Theta_D T_c^{-1}] \frac{\partial}{\partial r_s} \left( \frac{m^*}{m} a^2 \right) \frac{1}{2(1+a^2)} \\ & \left. + \ln^2 [0.85 \Theta_D T_c^{-1}] \frac{m^* a^2}{2m} \frac{\partial}{\partial r_s} (1+a^2)^{-1} \right\}. \quad (15) \end{aligned}$$

Using the fact that

$$\frac{m^*}{m} a^2 = n_F \frac{\pi e^2}{k_F^2},$$

where  $k_F$  is the magnitude of the wave vector at the Fermi surface and

$$\frac{\partial \ln n_F k_F^{-2}}{\partial \ln r_s} = \left[ \frac{\partial \ln n_F}{\partial \ln r_s} + 2 \right],$$

the derivatives are readily calculated. The result is

$$\begin{aligned} \frac{\partial^2 \epsilon(0)}{\partial r_s^2} = & \frac{\epsilon(0)}{r_s^2} \left\{ (K-1)K - (3\gamma + K) \right. \\ & - 2 \ln [0.85 \Theta_D T_c^{-1}] (3\gamma + K) \\ & + \ln^2 [0.85 \Theta_D T_c^{-1}] \left[ \frac{m^*}{m} \frac{a^2}{2(1+a^2)} \right] \left[ \frac{\partial \ln n_F}{\partial \ln r_s} + 2 \right] \\ & \left. - \ln^2 [0.85 \Theta_D T_c^{-1}] \left[ \frac{m^*}{m} \frac{a^4}{2(1+a^2)^2} \right] \right\}, \quad (16) \end{aligned}$$

where

$$K = \frac{\partial \ln \epsilon(0)}{\partial \ln r_s}.$$

As an example of the magnitude of this derivative for a real metal, Eq. (16) will be evaluated for indium

using the data given by Morel:

$$\begin{aligned} \frac{\partial \ln n_F}{\partial \ln r_s} = & 5.1_\gamma \ln^2 [0.85 \Theta_D T_c^{-1}] \left[ \frac{m^*}{m} \frac{a^2}{2(1+a^2)} \right] = 2.3, \\ -3\gamma = & -7.1, \quad a^2 = 0.40, \quad K = 19.7, \\ \Theta_D = & 109^\circ \text{K}, \quad T_c = 3.37^\circ \text{K}. \end{aligned}$$

The five terms in Eq. (16) are 368,  $-13.8$ ,  $+16.3$ ,  $-0.66$  and  $-0.82$ , respectively. It can be seen that the strongly dominant term is  $K(K-1)$ . The dominance of the first term seems to be the case for the other superconductors for which Morel's equation gives a result in agreement with experimental data. Since

$$\frac{\partial \epsilon(0)}{\partial y} \simeq -\frac{\epsilon(0)}{l} \left[ \frac{1}{3} K + \frac{1}{3} K(K-1) \frac{y}{l} \right], \quad (17)$$

then  $P = -\frac{1}{3}K$  and  $Q \simeq -\frac{1}{3}(K-1)K$ . For indium,  $P = -6.6$  and  $Q = -123$ . For a simple free-electron gas, one would expect  $[\partial \ln n_F / \partial \ln r_s] = -1$ ; however, Olsen and Rohrer<sup>13</sup> have shown that for real metals

$$\partial \ln n_F / \partial \ln r_s = 3(g-1),$$

where  $g$  is a constant which is determined experimentally. It is assumed that  $(\partial n_F / \partial y)$  can be determined by expansion in powers of  $(y/l)$  to give

$$\frac{\partial n_F}{\partial y} = \frac{1}{3} \left[ \frac{n_F}{y} - 3(g-1) \right] \left[ 1 + \frac{y}{l} \right]. \quad (18)$$

Then  $A = B = g-1$ ; for indium  $g-1 = 1.7$ .  $c^2$  can be rewritten as

$$\begin{aligned} c^2 = & -\frac{H_c^2(0)}{8\pi\rho_0} [B + 2Q] \\ & \times \left\{ 1 - \left( \frac{4Q - \beta B}{2Q + B} \right) \left( \frac{T}{T_c} \right)^2 + \left( \frac{2Q - B}{2Q + B} \right) \left( \frac{T}{T_c} \right)^4 \right\}, \quad (19) \end{aligned}$$

or

$$c^2 = c_0^2 [1 - bT^2 + aT^4]. \quad (20)$$

For indium,  $\rho_0 \sim 10^{-5}$  g cm<sup>-3</sup> and  $H_c(0) \sim 300$  Oe. Hence,  $c_0 \sim 10^5$  cm sec<sup>-1</sup>. The term  $F_n(T_c)$  for indium is approximately  $10^5$  ergs cm<sup>-3</sup>, while  $H_c(0)(8\pi)^{-1}$  is approximately  $3 \times 10^8$  ergs cm<sup>-3</sup>. Therefore, the temperature coefficients are  $a \sim 0.010$  and  $b \sim 0.19$ . It can be seen that in this calculation the temperature function is positive for all temperatures below  $T_c$ ; therefore, there exists a real velocity of propagation for a compressional wave in the superconducting electron gas.

Consider a slab of superconducting material of thickness  $l$  in the direction of propagation. One would expect a discrete set of standing wave modes for these com-

<sup>13</sup> J. L. Olsen and H. Rohrer, *Helv. Phys. Acta* **30**, 49 (1957).

pressional waves. If the boundaries are fixed, then the harmonic modes are given by  $\nu_n = n\nu_0[1 - bT^2 + aT^4]^{1/2}$ ; if the boundaries are free,  $\nu_n = (2n+1)\nu_0[1 - bT^2 + aT^4]^{1/2}$  where  $\nu_0 = c_0(2l)^{-1}$  and  $n$  is a positive integer.

Although the electrons are capable of density modulations relative to a fixed lattice, these modulations require that the electrons be dragged accordingly. It would not seem unreasonable, therefore, to suppose a direct interaction between lattice phonons and the collective excitation modes. It would appear likely that there would be a maximum exchange of energy from a compressional ultrasonic wave to the electron gas when the sound frequency,  $\nu_s$ , is equal to the frequency of one of the harmonic standing wave modes. Thus, absorption peaks would occur at temperatures for which  $\nu_s = \nu_n$ .

The ultrasonic absorption measurements which are made in single phase, soft superconductors usually involve a path length on the order of 1 cm or more. For indium, a 1-cm thickness implies  $\nu_0 \sim 10^5 \text{ sec}^{-1}$ . In the discussion of the data it will be shown that the energy absorbed from the sound wave decreases rapidly with the order of the harmonic. A sound frequency of  $10^7 \text{ sec}^{-1}$  is of the order of the 100th harmonic; therefore, the energy absorbed via this mechanism is negligible in the megacycle frequency range. If, however, there are smaller regions within a bulk superconductor which have altered superconducting properties so that there are separate superconducting phases present, it would be possible to have fundamental excitation modes in the megacycle frequency region.

### Hard Superconductors

A hard superconductor, in general, has a high-strain content arising from both impurities and dislocations. The various theories for the current-critical field behavior of a hard superconductor suppose that if the applied magnetic field exceeds the bulk critical field, the strained regions act as nucleating centers for the formation of smaller regions capable of sustaining a supercurrent. As has been pointed out, the strain fields also alter the local superconducting parameters such as the energy gap.

An idealized hard superconductor can be represented as consisting of uniformly spaced regions of strained and unstrained material. Initially, a semi-infinite slab of alternating layers of strained (modified) and unstrained (unmodified) materials will be considered. The thickness of a region is taken to be  $2r_0$ . All magnetic fields are assumed to be excluded from the interior regions. For simplicity, the strain fields are taken to be uniform throughout the modified regions. There will be an interfacial energy at the boundary between the modified and unmodified phases. Presumably, the location of the phase boundary is such as to minimize the electronic free energy subject to the constraints of the system. The interfacial energy should depend on the difference in energy densities between the two phases. The total

free energy of a system containing one modified and one unmodified region is of the form

$$F = F_{s1} + F_{s2} - S\mathcal{G}(H_{c1}^2 - H_{c2}^2), \quad (21)$$

(where  $S$  is a characteristic length) plus possibly a surface term involving the difference in normal electronic free-energy density. It can be seen that the derivative of the total free energy with respect to a displacement of the phase boundary yields a restoring force acting on the boundary having a temperature dependence which is a quadratic in  $T^2$ , similar to Eq. (12). Actually, the initial report of this absorption phenomenon included an attempt to derive the resonance condition in terms of this restoring force on the boundary. The hydrodynamic approach of the present paper, however, is an improved description of the actual physical situation. The role of the restoring force on the phase boundary in ultrasonic absorption is discussed below.

For the two-phase system, one would expect two sets of discrete standing wave modes for the collective excitations. The fundamental frequencies will depend upon the extent of the phase and the parameters which determine the velocity of propagation as in the single phase calculation. In the real, hard superconductor, the strain fields are those associated with defects such as dislocations and impurities. The extent of such strain fields is small in general, e.g., the order of  $10 \text{ \AA}$ . Due to the nonlocal nature of the superconducting state, interactions over distances less than the coherence distance  $\xi$  must be greatly reduced. It will be postulated that the interaction responsible for the collective excitations is reduced by the empirical function  $\chi(r_0) \equiv r_0 \xi^{-1} \exp(\alpha - \xi r_0^{-1})$ , where  $\alpha$  is a constant of order unity and  $2r_0$  is the extent of the phase in the direction of propagation. The function  $\chi(r_0)$  is one of the simplest forms that could be assumed; it will be shown that this function leads to results in good agreement with the Nb-Zr data. In addition, it has been shown by one of the authors<sup>14</sup> that  $\chi(r_0)$  leads to a prediction for the solute concentration dependence of the transition temperature in dilute superconducting alloys which is in remarkably good agreement with data for various solutes in Sn, In, and Al.

The complete expression for the fundamental collective excitation mode in one of the small strained regions with fixed phase boundaries is

$$\nu = \nu_0[1 - bT^2 + aT^4]^{1/2}, \quad (22)$$

where

$$\nu_0 = \frac{H_c(0)}{4\xi} \left[ \frac{-B - 2Q}{8\pi\rho_0} \right]^{1/2} \exp[\alpha - \xi r_0^{-1}],$$

$$a = \frac{2Q - B}{(2Q + B)T_c^4},$$

<sup>14</sup>L. T. Claiborne, J. Phys. Chem. Solids (to be published).

and

$$b = \frac{4Q - \beta B}{(2Q + B)T_c^2}. \quad (23)$$

Gibbons and Renton<sup>15</sup> have considered the conditions for isothermal compression over a length  $l$  in a metal. The time required to establish thermal equilibrium is

$$t = Cl^2/8\kappa, \quad (24)$$

where  $C$  is the specific heat in  $\text{J cm}^{-3}$ , and  $\kappa$  is the thermal conductivity in  $\text{W } (^\circ\text{K})^{-1} \text{cm}^{-1}$ . In terms of a compressional wave in a solid medium, the frequency at which the crossover from isothermal to adiabatic conditions occurs is

$$\nu_c = Cc^2/16\kappa, \quad (25)$$

where the appropriate length is one-half the wavelength of the sound wave. For a compressional mode in the electron gas, the electronic specific heat must be used. It should be noted that when one considers the adiabatic and isothermal conditions for a fixed length, the high-frequency processes are adiabatic, while the low-frequency processes are isothermal. When the length under consideration is one-half the wavelength of a sound wave, which is inversely proportional to the frequency, the situation is reversed. The thermal relaxation time decreases as the inverse square of the frequency so that high frequencies imply isothermal conditions and low frequencies imply adiabatic conditions. For indium, the electronic specific heat at the transition is approximately  $5 \times 10^{-4} \text{ J cm}^{-3}$ , the thermal conductivity is approximately  $8 \text{ W } ^\circ\text{K}^{-1} \text{ cm}^{-1}$ ; thus the cross-over frequency is  $\nu_c \sim 4 \times 10^4 \text{ sec}^{-1}$ . Consequently, the higher harmonics of the collective modes for the 1-cm-thick indium sample are isothermal. The isothermal conditions for the Nb-Zr system will be considered in the discussion below.

### Intermediate State

There is one other situation in which it might be possible to observe collective modes ultrasonically. If in the intermediate state there is a number of strata of superconducting material having approximately the same thickness  $d$  in the direction of propagation, then there is a possibility that a discrete set of collective modes exists which can be excited ultrasonically. The free-energy density is altered somewhat in the superconducting phase of the intermediate state, but one would expect the fundamental frequency to be temperature-dependent and inversely proportional to  $d$ . At a fixed temperature the frequency would be determined by  $d$ , which is, in turn, determined by the applied magnetic field  $H$ . Although the details of the calculation are not presented here, one can see that ultrasonic resonance peaks as a function of magnetic field should be expected.

<sup>15</sup> D. F. Gibbons and C. A. Renton, Phys. Rev. **114**, 1257 (1959).

Recently, Leibowitz and Chandrasekhar<sup>16</sup> have reported an oscillatory dependence of the ultrasonic absorption on magnetic field in the intermediate state which cannot be entirely attributed to the normal magnetoacoustic effect. At this time, their data have not been compared with a calculation such as has been indicated here; however, it does seem that the excitation of collective modes is a distinct possibility as the source of this oscillatory absorption behavior.

### DISCUSSION OF DATA AND THEORY

A study of the data for the 1% Zr sample such as the  $16.5 \text{ Mc sec}^{-1}$  data of Fig. 1 indicated that there were three sets (small, medium, and large) of absorption peaks present. According to the present model, each set of peaks represents consecutive harmonics of the temperature-dependent fundamental mode of collective excitation for one type of superconducting phase. The temperatures at which the maxima occur should be determined from either  $\nu_s = n\nu$  for fixed boundaries, or  $\nu_s = (2n+1)\nu$  for free boundaries, where  $\nu_s$  is the sound frequency and  $\nu$  is determined from Eq. (22).

The constants  $\nu_0$ ,  $a$ ,  $b$ , and the order of one of the harmonics are determined from the data at one measurement frequency. The results obtained from fitting the experimental data for the 1% Zr sample at one frequency are given in Table I for each of the three sets of

TABLE I. Experimental values of the three sets of constants.

	Small	Medium	Large
$\nu_0 (\text{Mc sec}^{-1})$	0.237	6.563	10.5
$a (^\circ\text{K}^{-2})$	0.000125	0.00210	0.000316
$b (^\circ\text{K}^{-4})$	0.0209	0.0849	0.0575

peaks. The positions of the maxima for all other sound frequencies are correctly predicted by these constants. The order of the harmonics goes as  $n$ , indicating fixed boundary conditions.

If one assumes that the temperature spread of each absorption peak represents a frequency "band width" for the absorption, then the temperature spread of any harmonic can be predicted at any sound frequency from an experimental fit at a single-sound frequency. The fitting of the data and the prediction of the absorption at other frequencies are illustrated in Figs. 3 and 4. Curve (a) of Fig. 3 shows the data for  $16.5 \text{ Mc sec}^{-1}$ . Curve (b) is the composite curve of the interpolated absorption peaks drawn on line (c). Except for the base line, which is a monotonically decreasing function of temperature, the interpolated absorption peaks of line (c) reproduce the quantitative positions of the data as well as the qualitative shape of curve (a). The test of the

<sup>16</sup> J. R. Leibowitz and B. S. Chandrasekhar, Bull. Am. Phys. Soc. **8**, 308 (1963).

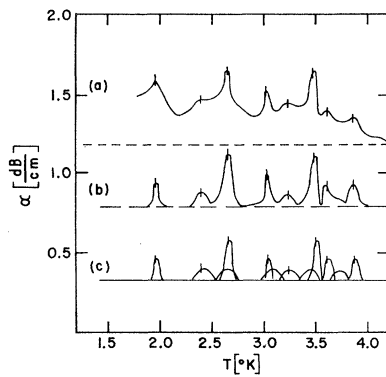


FIG. 3. (a) Experimental curve—attenuation versus temperature at 16.5 Mc sec<sup>-1</sup> in Nb-1.0% Zr alloy. (b) Composite theoretical curve. (c) Interpolated maxima.

interpretation is to predict the data for the same sample at other sound frequencies. In Fig. 4 on line (c) the predicted peaks at 10.0 Mc sec<sup>-1</sup> are plotted, keeping the relative amplitudes of the three sets of peaks the same as for 16.5 Mc sec<sup>-1</sup>. The composite predicted curve (b) agrees remarkably well with the data of curve (a). Again there is a base line shift which is not accounted for. The agreement of the composite predicted curves for the other frequencies for which data were taken in the same sample is equally good. Consequently, there seems to be a strong experimental verification of the resonance condition. An additional qualitative feature of the data is the dependence on  $n$  of the amplitude and width of the peaks. The amplitude seems to be a monotonically decreasing function of  $n$  while the frequency band width is relatively insensitive to the order of the harmonic. Taking into account the amplitude variation, the agreement between curves (a) and (b) of Fig. 4 would be even better. The amplitude dependence on  $n$  can easily be seen by comparing curves (c) and (d) of Fig. 1.

As was pointed out in the section on experimental results, some of the peaks were reduced in amplitude when the 1% Zr sample was annealed. The predicted composite curve for 12 Mc sec<sup>-1</sup> is given by curve (a) in Fig. 5. The data observed after 2 h of annealing are given by curve (b) in Fig. 5. It is readily noted that the medium and large peaks have been somewhat reduced in amplitude relative to the small peaks. If the amplitudes of the medium and large peaks are reduced by a factor of 2, the composite curve (c) results and the quantitative as well as the qualitative agreement is considerably improved. After an additional 16 h of annealing, all that remains of the "large" peaks are two small edges on the remaining small peaks, as can be seen in curve (d) of Fig. 5. An examination of curves (b) and (c) of Fig. 2 reveals that the small peak structure of the 1% Zr sample after an anneal time of 18 h is essentially the same as that for the 2.6% Zr sample after 16 h of annealing. The "medium" and "large" peaks are still in evidence in the 2.6% Zr sample data but have been greatly reduced.

Since the Zr ions and the dislocations are quite

likely to be randomly distributed, one would not expect any coherent resonance peaks to be associated with the unstrained niobium background. The small peaks are not affected by annealing; therefore, they must be due to some type of modified region which is fixed in the crystal. Perhaps the most obvious assumption would be that these peaks are due to the superconducting phases in the strain fields associated with the Zr ions. The medium and large peaks, however, must be associated with modified regions whose number is decreased by annealing, e.g., dislocations or grain boundaries.

At present, there is not sufficient information available about Nb to permit a complete evaluation of the theoretically predicted constants as given in Eq. (23). Some conclusions can be reached, however, regarding orders of magnitude and the relative sizes of the constants for dislocation strain fields compared with the strain fields associated with the presence of Zr ions in the Nb system. Assuming that  $Q$  and  $B$  are of approximately the same magnitude as calculated above for indium and that  $T_e$  and  $H_c(0)$  are approximately the same as for the unstrained pure niobium and using Eq. (23), then  $b = 0.026^\circ\text{K}^{-2}$  and  $a = 0.00015^\circ\text{K}^{-4}$ . From Table I it is seen that these values are of the correct magnitude and are, in fact, quite close to the experimental values for the small peaks. The fundamental frequency at absolute zero is  $\nu_0 \approx 10^6 \xi^{-1} \exp(\alpha - \xi r_0^{-1})$ . In an alloy, such as the 1% Zr sample, with high strain content, one would expect the coherence distance to be less than the penetration depth. A value of  $10^{-6}$  cm is probably a good estimate. Using the fundamental frequency for the small peak, and assuming that  $\alpha = 1$ , the extent of the strain field  $r_0$  can be estimated to be  $\sim 5 \text{ \AA}$ , about one lattice spacing, as would be expected for the strain field about an impurity ion. Making the

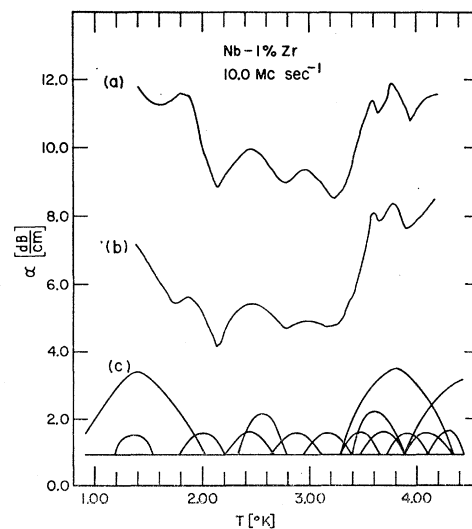


FIG. 4. (a) Experimental curve—attenuation versus temperature at 10.0 Mc sec<sup>-1</sup>. (b) Composite predicted theoretical curve. (c) Individual predicted peaks.



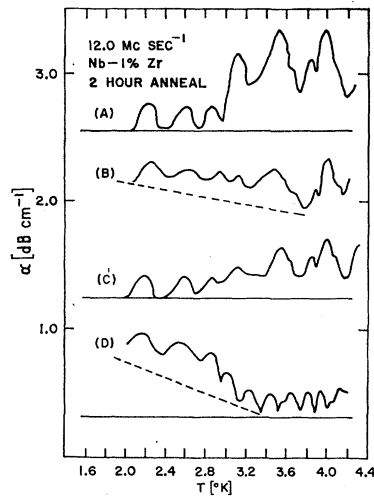


FIG. 5. (a) Theoretical curve previously obtained. (b) Experimental data after 2-h anneal. (c) Theoretical curve after reduction of large and medium size peaks. (d) Experimental data after 18-h anneal.

same assumptions, the fundamental frequency for the large peaks would imply an  $r_0 \sim 8 \text{ \AA}$ . Since it is expected that the strain field about a dislocation line is of greater extent than that about an impurity ion, it is seen that the variation of frequency with  $r_0$  is consistent with the interpretation of the source of the various sets of peaks.

The agreement of the theoretical estimate with the experimental values of  $a$  and  $b$  is quite good. However, the justification for the form of  $\chi(r_0)$  from the data is extremely qualitative. A much more quantitative justification for the reduction of the interaction constant for small strain fields by  $\chi(r_0)$  is given in the study<sup>14</sup> of the solute concentration dependence of  $T_c$  mentioned above.

An additional qualitative feature which might be discussed in terms of the phenomenological ideas presented in this development is the temperature dependence of the background attenuation. Even though the phase boundaries do not seem to move with the collective modes in a first approximation, it is still possible that the interaction of the compressional sound wave and the local strain field does work against the restoring

forces acting on the phase boundary. If this force is dissipative, the energy lost from the sound wave is proportional to  $F_r$  and would have a temperature dependence similar to that for  $c^2$ . From the magnitudes of  $a$  and  $b$  for niobium, it can be seen that this function is monotonically decreasing for  $T < T_c$ . Such a mechanism for the absorption of sound energy will be amplitude and frequency dependent. More experimental data are necessary before this possibility can be studied thoroughly.

### CONCLUSION

The collective excitation modes discussed herein are similar to the low-frequency collective modes introduced by Anderson and Bogoliubov except that the present calculation is made from a phenomenological viewpoint for a finite superconducting phase. The basic assumptions that the long-range Coulomb forces can be ignored, and that the electron distribution can be treated as a neutral Fermi gas are common to both treatments. An attempt was made to introduce the features of the superconducting state into the hydrodynamic treatment through the use of Morel's equation relating the superconducting parameters to volume or density changes. The resultant temperature dependence of the excitation modes is in good agreement with the interpretation of the data for the Nb-Zr system. A more fundamental calculation of the collective excitation modes for the electron distribution in a finite phase should be made. At this point it is evident that ultrasonic absorption measurements are a particularly direct method for studying the microstructure of hard superconductors. Further work along these lines is now in progress.

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