OSCILLATORY BEHAVIOR OF ULTRASONIC ATTENUATION IN SUPERCONDUCTING Nb-Zr ALLOYS

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(Received 4 December 1962)

A detailed account of the interaction between elastic waves and the conduction electrons in a pure metal has been given by Morse.[1] 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 attenuation for such materials, hence, no interesting phenomena at low temperatures. We have made measurements of the attenuation of ultrasonic compressional waves in zero applied magnetic field in 99.9% pure niobium and in two niobium-zirconium alloys at four frequencies between 5 and 30 Mc sec^{-1}, and it was found that there are striking variations of the attenuation as a function of temperature in the superconducting state. A definite structure of maxima and minima in absorption as a function of temperature was found in alloys of niobium with 1% zirconium and with 2.6% zirconium. An increase in absorption as the temperature was lowered, with some slight structure superimposed, was found in a 99.9% pure niobium polycrystal. Some of the experimental results are shown in Fig. 1; the attenuation measurements were made using the technique described by Chick, Anderson, and Truell.[2] The fact that the observed structure is a property of the superconducting state was established by applying a sufficiently large magnetic field (>20 kG) to destroy the superconducting state and observing that the structure disappeared. It was also observed that there was little structure in the shear wave attenuation. Thus for the superconducting state in niobium and niobium-zirconium alloys there must exist some temperature-dependent mechanism for the absorption of energy from an ultrasonic wave. The following conclusions were reached in regard to this mechanism: (1) It is a property of the superconducting state. (2) It is probably related to pressure and/or charge density modulations. (3) It is strongly frequency dependent. (4) It is not dependent on the amplitude of the sound wave at small strains in the frequency range studied.

The present theories of hard superconductors which have been developed to account for their high current-carrying capacity in the presence of large magnetic fields are based on the breakdown of the material into superconducting and

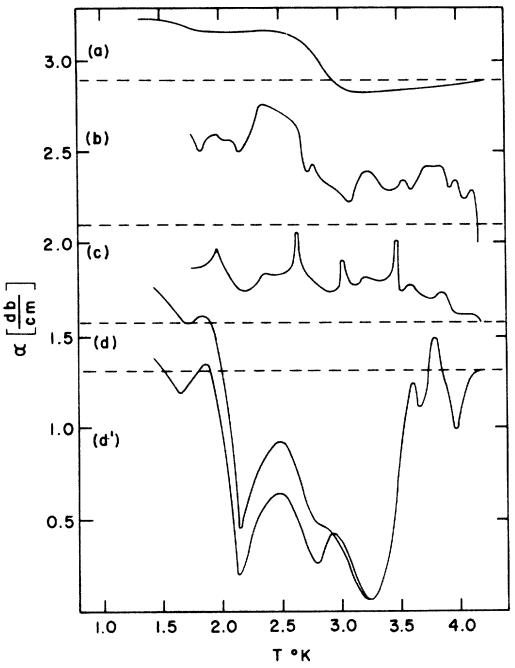

FIG. 1. (a) Attenuation (dB cm^{-1}) at 10 Mc sec^{-1} as function of temperature for 99.9% pure Nb. (b), (c), and (d) Attenuation (dB cm^{-1}) as function of temperature in Nb-1% Zr alloy for 29.0, 16.5, and 10.0 Mc sec^{-1}, respectively. (d') Data of curve (d) with background (a) removed.

normal regions when a critical field is exceeded. The model of Hauser and Buehler[3] asserts that the current can be carried along filaments, centered about dislocation lines, which are smaller in diameter than the magnetic field penetration depth and which remain superconducting after the bulk material becomes normal. It should be noted, of course, that the dislocation lines and other modifications of the crystal are always present within the material, and the superconducting parameters such as the energy gap will have local variations even when all fields are excluded by diamagnetism. The negative surface energy model for hard superconductivity due to Goodman[4] gives no microstructure except in a field greater than the critical field; therefore, it is not applicable here.

Consider the simple picture of a block of soft superconducting material of critical temperature

T_{c1}, critical field H_{c1}, and energy gap Δ_1, with cylinders of radius $\sim 10^{-7}$ cm of modified material running through it perpendicular to the direction of propagation of the sound wave. In the region of the strain field, there will be a modified transition temperature and energy gap; thus, we can assign a modified bulk thermodynamic critical field, and further simplify the model by considering the average values of these parameters (T_{c2}, H_{c2}, Δ_2) to be uniform within the strain field. What we have developed, then, is a system of two types of superconducting material separated by a phase boundary. The action of each filament under an impressed sound field can be considered separately, provided the density of filaments is sufficiently low that the separation distance is greater than the penetration depth.

The free energy of the system can be written as the sum of the free energies of a filament, its surrounding unstrained material, and the interface between the two phases. At equilibrium, the free energy of one filament and its environment is

$$G_s = -(H_{c1}^2/8\pi)V_1 - (H_{c2}^2/8\pi)V_2 + \xi(H_{c1}^2 - H_{c2}^2)A,$$

where V_1 and V_2 are the volumes of the two types of superconducting materials, A is the interfacial area, and ξ is the characteristic length associated with the surface energy; the surface energy term vanishes for a uniform superconductor. The two assumptions made here are that the phase boundary is established in such a way as to minimize the free energy, and that the surface energy is a linear function of the squares of the two critical fields. The latter assumption seems reasonable in view of the results[5] for the surface energy between a normal and superconducting region. For a displacement δx of the phase boundary in the direction of the sound wave, there will be a restoring force $F = -\partial G_s/\partial x$ which is linear in x to first order.

When a compressional wave propagates through the system, the cylinder will be distorted by the pressure gradient, but the number of electrons contained within the phase will be unchanged in order to preserve charge neutrality. There results a change in the energy gap and a shift of the phase boundary. The restoring force on the phase boundary acts through the electron distribution and not directly on the lattice system. Considering the fact that the electrons and the lattice are loosely coupled, one can see that there is a fundamental mode of vibration for the phase boundary between the electron distributions; this vibration might be thought of as a type of plasma oscillation.

For a particular geometry of the modified phase, one can find resonance conditions for vibrations of the electron gas at the fundamental and higher harmonics. However, it can be shown that the general result for the temperature dependence of the fundamental, the form of which is independent of geometry, is

$$\omega_f = \omega_0(1 - bT^2 + a\,T^4)^{1/2}.$$

The resonance condition occurs whenever the frequency of the sound wave, ω_s, is an integral multiple of the fundamental, $\omega_s = n\omega_f$. The constants a and b depend upon the ratios of the fundamental parameters of the unmodified to those of the modified material. ω_0, however, depends also on the geometry and will be different, for instance, for dislocation lines than for spherical regions about impurity ions.

We shall now show that the result of this derivation completely explains the appearance of the absorption maxima and qualitatively explains the detailed shape of the experimental curves. A detailed calculation and its application to other alloys will be presented elsewhere.

Examination of the data for the 1% Zr alloy reveals that there are three sets of absorption peaks present with different temperature dependences and different relative amplitudes. The constants describing the three sets of absorption peaks can be determined at a given ultrasonic frequency, then the positions of the maxima for the data at other frequencies can be predicted; the results are presented in Table I.

The manner in which the qualitative shapes of the curves are reproduced is shown in Fig. 2. Similar theoretical curves are obtained for the other frequencies. If one notes the approximate

Table I. Summary of results for Nb-Zr system.[a]

ω_0 (Mc sec^{-1})	a [(°K)$^{-4}$]	b [(°K)$^{-2}$]
4.119	12.28×10^{-4}	6.029×10^{-2}
1.3900	3.74×10^{-4}	4.441×10^{-2}
0.2372	1.25×10^{-4}	2.090×10^{-2}

[a]The calculated values for a cylinder of radius 10^{-7} cm, $H_c(0)$ of 2×10^3 G (see reference 6), and T_c of 10°K are $\omega_0 = 2$ Mc sec^{-1}, $a = 10^{-4}$ (°K)$^{-4}$, and $b = 10^{-2}$ (°K)$^{-2}$.

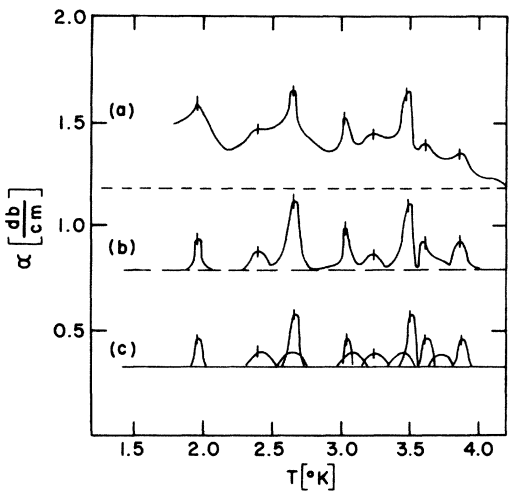

FIG. 2. (a) Experimental curve—attenuation vs temperature at 16.5 Mc sec^{-1} in Nb-1% Zr alloy. (b) Composite theoretical curve. (c) Theoretically predicted maxima.

width of the peaks for one frequency, then one can calculate as well the widths at other frequencies. For example, if the width is assumed to be due to a spread in fundamental frequencies, as would appear reasonable, then the peaks would occur in the interval $n(\omega_0 \pm \delta\omega_0)(1 - bT^2 + aT^4)^{1/2}$ for fixed n, a, and b. The width can then be calculated for any other sound frequency. This analysis reproduces the observed broadening of the maxima at lower frequencies.

The results of this experiment indicate that ultrasonic measurements on hard superconductors can lead to detailed information on the microstructure of these materials and on the relationship between the microstructure and the bulk mechanical and electromagnetic properties. Experiments are currently being conducted in order to relate controlled modifications of the microstructure of Nb-Zr and other hard superconducting alloys to the behavior in a magnetic field.

The authors acknowledge with thanks many stimulating conversations with R. Stratton, the helpful comments of Professor H. E. Rorschach, the efforts of C. D. Wiseman in preparing the materials, and the able assistance of J. L. Rooke.

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LATTICE DISTORTIONS IN A $SrTiO_3$ SINGLE-CRYSTAL ELECTRET*

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(Received 2 November 1962; revised manuscript received 29 November 1962)

In recent years, several polycrystalline inorganic substances have been found to exhibit permanent surface charges after being polarized at room temperature in a strong electric field.[1-3] These so-called electro-electrets need not be short-circuited to maintain their surface charges for long periods of time, as is necessary with thermo-electrets like carnauba wax, etc. Besides, some of the ceramic electrets did not show a change in polarity, thus indicating that the effective surface charge apparently is caused predominantly by the heterocharge of permanent dipole moments in the substance; however, considerable fluctuations of the effective surface charges were observed, both in substances with and without change in polarity.

In order to study the nature of the heterocharge, experiments with single-crystal electrets were started, the preliminary results of which are described in this note. For these experiments strontium titanate was used. This substance had been reported to form an electret in the polycrystalline state.[3] A 4-mm thick slab was cut from a large single-crystalline boule[4] and polarized perpendicularly to its (110) surfaces in an electric field of about 30 kV/cm.

By means of Laue back-reflection photographs, the structure of the sample then was investigated at various periods of time after electrification. A first run, in which the incident x-ray beam was parallel to the direction of the polarizing field, revealed a shift of individual Laue spots