Temperature dependence of the velocity of ultrasound in superconducting tin

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Data are presented on the variation of the velocity of high-frequency ultrasonic waves in the superconducting transition in tin. It is shown that near T_c the contribution to the velocity of transverse sound is satisfactorily described by the Ozaki and Mikoshiba theory.[5] Far from T_c, the major effect on the velocity is exerted by the dislocation structure of the sample. An anomalous behavior of the quantities measured is observed in samples with a sound wave vector $\mathbf{q} \parallel [110]$ and polarization $\epsilon \parallel [110]$.

Until recently, ultrasonic investigations of superconductors consisted mainly of experiments to study the temperature dependence of sound absorption, which has a major role both in the verification of the fundamental propositions of the microscopic theory of superconductivity[1] and in its further development. It suffices to recall that the existence of gap anisotropy in a pure single-crystal superconductor was first most convincingly demonstrated precisely in experiments to study the dependence of the temperature behavior of the high-frequency ultrasonic absorption coefficient on the orientation of the sound wave vector **q**.

So far as the velocity of sound at the superconducting transition is concerned, this problem has been studied less intensively in both its theoretical and experimental aspects. At the same time, it is known that the changes in the sound velocity at the superconducting transition, although small, are entirely observable and therefore it is to be hoped that their investigation will give additional information on the properties of the superconducting state.

At the present time, at least three mechanisms are known which affect the sound velocity in superconductors. First, a rearrangement takes place in the phonon spectrum of a metal at the superconducting transition. As a result, the velocity of the ultrasonic waves changes. Effects of a similar nature should be observed both in real crystals and in an ideal lattice for waves of any frequency. Theoretical calculations[2,3] and experimental data[4] show that the corresponding relative change in the velocity amounts to several parts per million.

Second, for transverse ultrasonic waves of high frequency ($ql > 1$, **q** is the sound wave vector, l the free path of the electrons), dynamic effects are observed near T_c that are connected with Meissner screening of the electromagnetic fields that accompany the propagating wave. They lead to a stronger ($\sim 10^{-4}$) change in the sound velocity than in the first case. The effect was predicted theoretically in[5,6] and observed experimentally in[7,8]. This effect should also take place in both nonideal and ideal crystals.

Third, there is in any real crystal a dislocation contribution to the elastic modulus, and inasmuch as the superconducting transition changes the dynamic characteristics of the dislocation structure of the sample (as a consequence of lowering of the electron viscosity), then corresponding changes in the sound velocity should be observed here. In crystals with small amounts of impurities, this mechanism should also result in dependences much stronger than in the first case.

A systematic investigation of the changes in the velocity of longitudinal and transverse ultrasonic waves was carried out in the present study for a pure single crystal of tin for all the principal directions of propagation and for all possible sound polarizations. The experimentally observed dependences indicate that the principal contribution to the change in velocity in our case is made by the second and third mechanisms.

EXPERIMENTAL METHOD

Generally speaking, it is desirable to study the changes in the velocity of ultrasound simultaneously with study of absorption. This is because these data complement one another and make the analysis of the experimental results easier. In this connection, the measurement apparatus employed by us allowed simultaneous and automatic study of both velocity and absorption changes. Detailed information on the apparatus has been published elsewhere,[9] and therefore we shall not touch on the specific details of the equipment here. It consists of an acoustic bridge that is self-balancing in two parameters and operates in a pulsed mode. The accuracy of the absorption measurements is $\sim 10^{-3}$, and that of the velocity measurements $\sim (2-3) \times 10^{-6}$.

The use of such apparatus has a whole series of advantages in comparison with that used in[7,8]. First, there is the possibility of simultaneous recording of both parameters which characterize the sound propagation. Second, there is the high efficiency in measurements on samples with large absorption. This made it possible to operate at high frequencies (or to use long samples for the study of dislocation effects). Third, there is the independence of the experimental results of the quality of the screening of the sample in the case of pulse measurements, in contrast with the resonance method used in[7,8]. All the measurements were carried out at frequencies of 51.4 and 154.2 MHz.

The samples were taken from OVCh-000 initial material with a resistance ratio $R(4.2°K)/R(300°K) \sim (3-4) \times 10^{-5}$, in the form of beads in a glass mold with subsequent electric-spark cutting by a thin copper wire. The given method of sample preparation introduced a small number of defects and assured the possibility of measurements on a single sample for all the principal directions of propagation. Some of the samples were annealed in a hydrogen atmosphere at a temperature of 210°C; however, no change was noted in the measured characteristics in this case, which indicates that few defects were introduced by the electric-spark cutting. The accuracy of orientation of the samples by means of x-ray methods was better than 1°. The pickups used for the longitudinal oscillations were plates of lithium metaniobate, cut at an angle of 57° in the yz plane, with a fundamental frequency of 51.4 MHz. The pickups for excitation of transverse waves were made from AC-cut quartz, with accuracy of the cut-angle setting better than 30 min.[1)]

The magnetic field on the sample was compensated to the level of 3—5 mOe with the help of three pairs of Helmholtz coils and controlled by a ferro-probe pickup. Local uncontrolled variations of the magnetic field on the sample also amounted to no more than 3 mOe.

LONGITUDINAL WAVES

The first measurements of the change in the velocity of longitudinal ultrasonic waves at the superconducting transition in the case of high sound frequencies ($ql \gtrsim 1$) were performed in[7,8]. The authors found that in tin these changes amount to 2×10^{-4} and in lead to 3×10^{-4}. The temperature dependence of the velocity is similar to the temperature behavior of the absorption, in accord with the theory of Bardeen, Cooper and Schrieffer[1] it was suggested that these velocity changes were connected with the direct effect of the electron gas on the dynamic elastic moduli of the ideal lattice.

The data of the present work contradict this hypothesis. Actually, it turned out that the results of the measurements of the velocity change of a longitudinal ultrasonic wave do not repeat themselves in different cooling cycles of a given sample, but depend on its previous history. The explanation of these phenomena should evidently be associated with the dislocation nature of their origin. Here, inasmuch as the measured quantities do not depend on the amplitude of the sound field over a sufficiently broad range of values, the determining mechanism is the mechanism of frequency-dependent internal friction. A simple theory of this phenomenon is contained in the work of Granato and Lucke.[10]

According to[10], the contribution to the ultrasonic velocity due to dislocations is described by the expression

$$\frac{V-V_0}{V_0}=k\frac{\omega^2-\omega_0^2}{(\omega^2-\omega_0^2)^2+(\omega d)^2}, \quad (1)$$

where k is a constant dependent on the density of mobile dislocations and on the material of the sample; ω is the sound frequency, ω_0 the effective resonance frequency of the dislocation structure, and d the constant of dislocation damping, which depends on the viscosity of the electron gas.

It is reasonable to assume that the only parameter which changes at the superconducting transition is the quantity d, which decreases upon a decrease in the temperature, as a consequence of the decrease in the number of normal excitations in the superconductor. It is not difficult to see that for $\omega < \omega_0$, the contribution of the dislocations to the sound velocity is negative and increases in absolute magnitude upon a decrease in d, which corresponds to a decrease in the experimentally measured sound velocity at the superconducting transition. Correspondingly, the measured value of $\Delta V/V$ for $\omega > \omega_0$ will have a positive sign.

Inasmuch as for practically all samples the sound velocity decreases below the transition temperature in the same way as in[7,8], the conclusion should be drawn that the effective resonance frequency ω_0 for our samples is at least greater than 150 MHz.

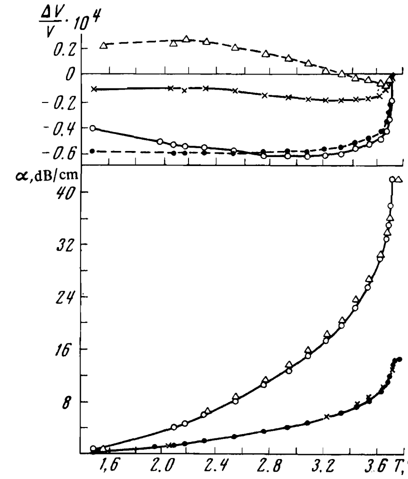

FIG. 1. Temperature dependence of the relative change in the velocity $\Delta V/V$ (upper figure) and the absorption coefficient α (lower) for a tin sample before deformation and after deformation in the case q ∥ [001]. Frequency 51.4 MHz: ●—before deformation; ×—after deformation; frequency 154.2 MHz: ○—before deformation; △—after deformation.

To test these hypotheses, we carried out experiments on freshly deformed samples, in which one could expect a lowering of the value of ω_0 due to the introduction of new dislocations with long loops that had not yet been pinned by the impurities. The results are shown in Fig. 1. It is seen that the deformation materially changes the behavior of the velocity below the transition temperature. It should be noted here that the absorption coefficient of the deformed sample is practically the same as that of the undeformed sample. This indicates a small change in the free path of the electrons in the deformation and, consequently, that the changes in the behavior of the velocity are not connected with changes in the quantity ql. The initial decrease in the velocity below T_c that is observed on all curves is evidently connected with the first mechanism mentioned at the beginning of the paper.

Whenever frequency-dependent internal friction appears in a sample, one should expect the appearance of amplitude-dependent losses upon an increase in the sound-field amplitude. Up to now, such losses have not been observed in superconducting tin. The reason for this is in all probability the large value of the amplitude of detachment of the dislocations from the pinning points. Thanks to the use of highly efficient pickups in our experiments, we succeeded in observing amplitude-dependent effects (Fig. 2). They appear more strongly in the behavior of the velocity than in the behavior of the absorption. This is connected with the fact that the accuracy of the relative measurements of the velocity in the given case appreciably exceeded the accuracy of the absorption measurements. So far as the absolute values of the changes are concerned, the change in the decrement in the case of amplitude-dependent internal friction $\Delta = (V/f)\alpha$ and the relative change in the modulus $\Delta E/E = 2\Delta V/V$ are the same in order of magnitude, as follows from theory.[10]

TRANSVERSE WAVES

It is known that in the case $ql \gg 1$, the absorption of transverse sound undergoes a sharp decrease by an

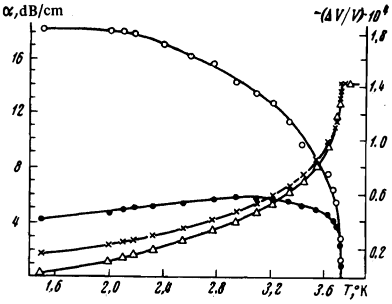

FIG. 2. Temperature dependence of ΔV/V and α for longitudinal ultrasound of frequency 51.4 MHz in the case q ∥ [001] and sound-field amplitudes that differ by 40 dB. For ΔV/V: ●—small amplitude; ○—large amplitude. For α: △—small amplitude, X—large amplitude.

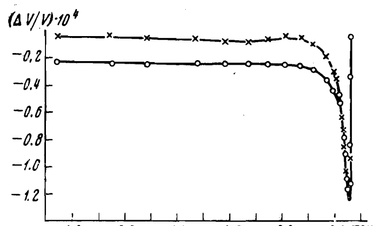

FIG. 3. Temperature dependence of ΔV/V for transverse sound of frequency 51.4 MHz for the case q ∥ [110] and ε ∥ [001]: ○—behavior after single cooling to the temperature of liquid helium; X—behavior after refilling with helium after a day of holding the sample at room temperature.

amount ~20—70% in a narrow range of temperatures $\Delta T/T_c \sim 0.01$. This effect is explained by the fact that in the normal state, for not too high frequencies, at which current neutrality is still preserved ($f \lesssim 10^9$ Hz), significant contributions are made to the sound absorption by the electromagnetic fields, screening of which as a consequence of the Meissner effect leads to an observable jump in the absorption. As was first pointed out by Ozaki and Mikoshiba,[5] the screening of electromagnetic fields should also lead to a rather large change in the velocity of the ultrasound near T_c. Such a change in the sound velocity has also been observed experimentally in[7] for $ql \sim 1$.

Typical curves for the experimental data taken on a single sample in different cooling cycles are shown in Fig. 3. The entire temperature range of the velocity changes can be divided into two intervals. One of these spans the temperature range ~0.1°K immediately below T_c; in this region, the results are reproducible, both for different cooling cycles and for different samples. The second interval spans the remaining temperatures down to 0°K, and the picture of the velocity behavior is entirely analogous to that described above for the longitudinal waves, i.e., the velocity changes observed in this region are connected with the dislocation mechanism of internal friction. In what follows, we shall consider only the region near T_c, inasmuch as it is directly connected with the superconducting properties of the sample.

In accord with the simplest model, which was put forth in[5], the absorption α and the velocity change ΔV/V of transverse waves in a superconductor are described by the following expressions:

$$\alpha = K/2\rho V, \tag{2}$$

$$\frac{\Delta V}{V} = \frac{1}{2}\left[\left(\frac{K}{2\rho\omega}\right)^2 + \frac{L}{\rho\omega}\right], \tag{3}$$

$$K = \frac{Nm}{\tau}\left[\frac{(1-ng)^2 ng}{(ng)^2 + (s/\omega\tau)^2} + (1-g)n\right], \tag{4}$$

$$L = \frac{Nm}{\tau}\frac{(1-ng)^2 s/\omega\tau}{(ng)^2 + (s/\omega\tau)^2}, \tag{5}$$

where $g(ql)$ is the Pippard function for the absorption of transverse waves, which can be set equal to $3\pi/4ql$ in our case, where $ql \gg 1$; N is the electron density, ρ the density of the metal, m the mass of the electron, and s and n are the concentrations of superconducting and normal electrons, respectively; $s = 1 - n$. The deformation part α_D, which must be subtracted from the total absorption in the treatment of the experimental data, does not enter into the absorption coefficient α.

On the substitution of the function K in (2) for the absorption, we obtain two components. One of them, which corresponds to the first term in the square brackets in Eq. (4), describes the electromagnetic absorption α_F, and the second is the collision term, which makes a contribution to the residual absorption α_{res} which, like α_D, must be subtracted from the total absorption.

We shall now assume that $g(ql) \ll 1$ (estimated value $ql \approx 50$), and close to T_c we have $n = 1$. Direct calculation also shows that $(K/2\rho\omega)^2 \ll L/\rho\omega$. In this connection, the formulas given above can be rewritten in the form

$$\alpha_E = \alpha - \alpha_{rest} = \frac{Nm\omega}{2\rho V}\left(\frac{3\pi}{4}\frac{V}{v_F}\right)\left[\left(\frac{3\pi}{4}\frac{V}{v_F}\right)^2 + s^2\right]^{-1}, \tag{6}$$

$$\frac{\Delta V}{V} = \frac{Nm}{2\rho}s\left[\left(\frac{3\pi}{4}\frac{V}{v_F}\right)^2 + s^2\right]^{-1}, \tag{7}$$

where v_F is the Fermi velocity.

A number of consequences follow from these formulas:

1. The quantity ΔV/V passes through a maximum at $s = (3/4)\pi V/v_F$. Taking this into account and assuming the concentration near T_c to be $s = 2\Delta T/T_c$, as follows from the microscopic theory of superconductivity, we obtain $\Delta T_{max}/T_c = 3\pi V/8v_F$.

2. The value of the maximum velocity change $(\Delta V/V)_{max} = Nmv_F/3\pi\rho V$.

3. The electromagnetic part of the absorption in the normal state is determined by the expression $\alpha_{En} = 2q(Nmv_F/3\pi\rho V)$.

4. The quantities α_{En} and $(\Delta V/V)_{max}$ are connected by the relation $\alpha_{En} = 2q(\Delta V/V)_{max}$.

5. The ratio of the measured quantities is $\Delta V/V\alpha_E = (8v_F/3\pi\omega)\Delta T/T_c = \mathscr{K}\Delta T$.

The experimental curves of α(T) and ΔV/V = f(T) are plotted in Fig. 4 for all the principal directions of propagation. Here we have also plotted the dependence of $\Delta V/V\alpha_E$ on the temperature, from which it is seen that the experimental points lie sufficiently close to a straight line. We recall that the quantities α and ΔV/V were recorded simultaneously; therefore the possibility of a shift of the α(T) and ΔV/V = f(T) curves relative to one another because of inaccurate determination of the temperature is completely eliminated.

A comparison of the basic parameters obtained from our curves with the calculated values is shown in the Table. In the calculations, the values of the sound velocities were taken from[11], N was taken to be equal to 4×10^{22} cm^{-1}, the mass m* was assumed equal to the mass of the free electron, and $v_F = 0.65 \times 10^8$ cm/sec.[1] The latter quantities are in some doubt since both the

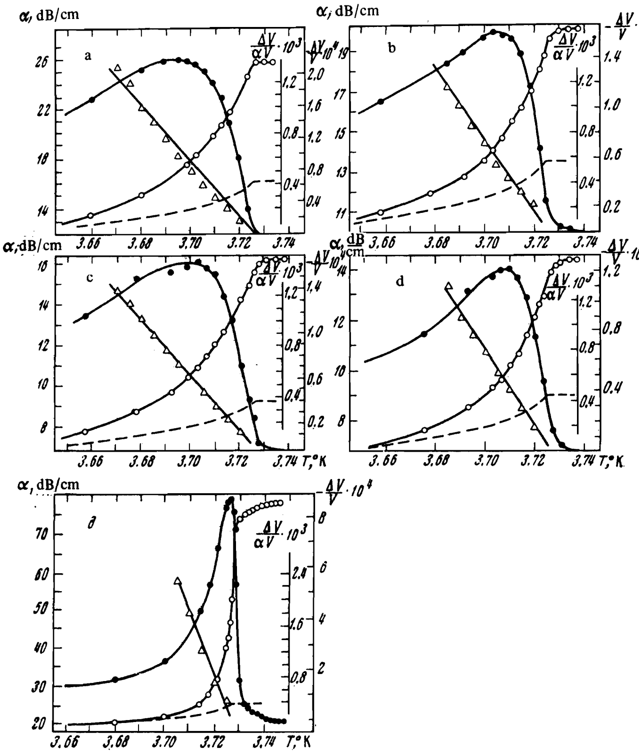

FIG. 4. Temperature behavior of $\Delta V/V$ and α for transverse sound of frequency 51.4 MHz for different orientations of q and ϵ: ●—$\Delta V/V$, ○—α, △—$\Delta V/\alpha V$ cm/neper; dashed curve—deformation part of the absorption. a—for the case q ∥ [001] ϵ ∥ [011]; b—for the case q ∥ [100], ϵ ∥ [001]; c—for the case q ∥ [100], ϵ ∥ [010]; d—for the case q ∥ [110], ϵ ∥ [001]; e—for the case q ∥ [110], ϵ ∥ [$\bar{1}$10].

effective mass and the Fermi velocity are anisotropic quantities. However, one can make reference here to the fact that the electromagnetic interaction is determined by the integral over the entire Fermi surface. Therefore, in the formulas given above, we should understand by the quantities m^* and v_F certain averages of them which do not differ strongly from those used in the calculation, and which are isotropic quantities.

If we do not at present take into account the results which pertain to the case in which **q** ∥ [110] and ϵ ∥ [$\bar{1}$10], for which the experimental data differ significantly from those calculated, then it is seen from the Table that the measured parameters are rather close to their calculated values. It is necessary here to take into account that the results of the calculations were obtained under the assumption of isotropy of the Fermi surface. For the quantities $(\Delta V/V)_{max}$ and in part α_{En}, the calculated values of which do not depend on the characteristics of the superconducting state, the agreement turns out to be quite good, and it is to be hoped that account of the anisotropy would lead to still better agreement between theory and experiment. So far as the quantities $\Delta T_{max}/T_c$ and $\mathscr{K}$ are concerned, the divergences here are larger. Evidently, these divergences are explained by the fact that the simplified theory[5] does not accurately describe the behavior of the absorption and the sound velocity near T_c.

Actually, according to the formulas given above, α and $\Delta V/V$ should have vanishing derivatives at the point T_c. In fact, a sharp change is observed in these quantities at the transition point and, as is seen from Fig. 4, $\alpha(T)$ and $\Delta V/V(T)$ have more or less sharply expressed

Orientation	$V\cdot 10^{-5}$ cm/sec	$\frac{\Delta T_{max}}{T_c}\cdot 10^3$		$\left(\frac{\Delta V}{V}\right)_{max}\cdot 10^4$		α_{En}, neper/cm		$\frac{\alpha_{En}}{\Delta V/V}\cdot 10^{-4}$ neper/cm		$\mathscr{K}\cdot 10^2$, cm/neper-deg	
		theory	experiment	theory	experiment	theory	experiment	theory	experiment	theory	experiment
q∥[100] ε∥[001]	1.92	3.5	5.6	1.76	1.59	0.59	0.76	0.335	0.478	4.6	2,85
q∥[100] ε∥[010]	1,96	3.6	7.0	1.72	1,63	0,57	0.81	0.331	0.498	4.6	2,22
q∥[001] ε∥[110]	1.92	3.5	8.3	1.76	2,20	0.59	1.10	0.335	0,500	4.6	2.23
q∥[110] ε∥[001]	1.92	3.5	4.8	1.76	1,22	0.59	0.63	0.335	0.515	4,6	3,10
q∥[110] ε∥[$\bar{1}$10]	1.31	2.4	0.54	2.57	8.70	1.26	6.04	0.490	0.694	4.6	10.50

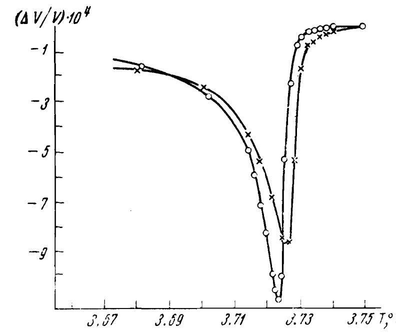

FIG. 5

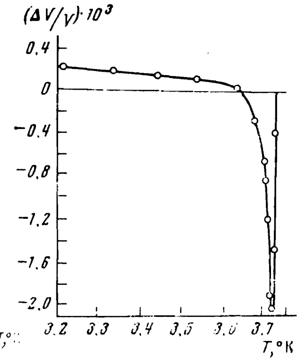

FIG. 6

FIG. 5. Temperature behavior of $\Delta V/V$ for transverse sound of frequency 51.45 MHz for the case q ∥ [110] and ϵ ∥ [$\bar{1}$10] in tin samples of different purity: X—pure sample; ○—dirty sample.

FIG. 6. Temperature behavior of $\Delta V/V$ for quasilongitudinal ultrasonic waves of frequency 154.2 MHz near T_c at q ⊥ (111).

singularities near T_c on all the curves. As for the smooth dependence observed for these quantities near T_c, their behavior is evidently explained by the specific fluctuations.[12]

The results of the measurements in indium[13] like the experimental data of the present paper, indicate that the derivatives of the quantities α and $\Delta V/V$ have discontinuities at T_c. A more accurate account of the parameters of the superconductor[13] allows us to remove this contradiction, and leads to significantly better agreement of theory with experiment. In our case corrections similar to those introduced in[13] should also bring the calculated values closer to the experimental data.

Under the conditions **q** ∥ [110], ϵ ∥ [$\bar{1}$10], the departures of the experimental values from the calculated ones are anomalously large. One can attempt to improve the agreement between them by assuming that in the given case we observe interaction with some group of electrons that have a Fermi velocity about three times that used for the calculations. However, the problem in fact turns out to be more complicated, since in the given orientation anomalous behavior of the sound absorption coefficient is also observed in the normal state.[14] Moreover, because of the large role of the fluctuations for the given group of electrons,[12] one should expect a significant change in the superconducting characteristics (for example, the concentration of superconducting electrons).

The behavior of the velocity of sound for the given orientation also differs materially from the theoretical conceptions for doped samples. Figure 5 shows the data on the velocity for pure tin with $R(4.2°K)/R(300°K) \approx (3-4) \times 10^{-5}$ and contaminated tin with $R(4.2°K)/R(300°K) \approx (3-4) \times 10^{-4}$. Contrary to expectations, the value of $(\Delta V/V)_{max}$ for the tin sample containing impurities turned out to be even larger than for the pure sample. We note that this fact is entirely in agreement with the behavior of the sound absorption coefficient in the normal state.[14]

It was noted earlier[15] that for compound cuts one should take into account the electromagnetic contribution to the absorption of the longitudinal waves, which, as in the case of transverse waves, leads to the appearance of a jump in the absorption near T_c. Our measurements of the velocity changes of such waves confirm this. Actually, the behavior of the velocity near T_c is determined to a significant degree by the electromagnetic interaction, which leads to effects that are characteristic for transverse waves (Fig. 6). Generally speaking, departure from a simple crystallographic cut by a few degrees is enough to lead to the appearance of a peak in the velocity below the transition temperature.

In conclusion, we take this opportunity to thank A. S. Pirogov and B. N. Aleksandrov for help in the preparation of the samples.

[1)]This was necessary to obtain a high degree of linearity of the ultrasound polarization ϵ.

[1] J. Bardeen and J. Schrieffer, New Developments in the Study of Superconductivity (Russian translation, Fizmatgiz, 1962).
[2] I. O. Kulik, Zh. Eksp. Teor. Fiz. **43**, 1489 (1962) [Sov. Phys.-JETP **16**, 1052 (1963)].
[3] J. Bardeen and M. Stephen, Phys. Rev. **136**, 1485 (1964).
[4] G. A. Alers and D. L. Waldorf, Phys. Rev. Lett. **6**, 677 (1961).
[5] H. Ozaki and N. Mikoshiba, Phys. Lett. **23**, 52 (1966).
[6] J. L. Stevens and A. Houghton, J. Phys. Chem. Sol. **31**, 1677 (1970).
[7] B. G. W. Yee and B. C. Deaton, Phys. Rev. Lett. **23**, 1438 (1969).
[8] B. C. Deaton, Phys. Lett. **32A**, 333 (1970).
[9] V. D. Fil', P. A. Bezuglyĭ, E. A. Masalitin and V. I. Denisenko, Pribory i Tekhn. Éksperim. No. 3, 210 (1973).
[10] A. Granato and K. Lucke, J. Appl. Phys. **27**, 583 (1956).
[11] J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. **120**, 1658 (1960).
[12] V. D. Fil', V. I. Denisenko, P. A. Bezuglyĭ and E. A. Masalitin, ZhETF Pis. Red. **16**, 462 (1972) [JETP Lett. **16**, 328 (1972)].
[13] K. Fossheim, Technical Report No. 685, University of Maryland, 1967.
[14] V. D. Fil', V. I. Denisenko and P. A. Bezuglyĭ, ZhETF Pis. Red. **18**, 340 (1973) [JETP Lett. **18**, 200 (1973)].
[15] J. M. Perez, Canad. J. Phys. **44**, 1765 (1966).

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