

with GL occurs in the type-II alloy near T_{c2} ; this is reasonable since as one approaches T_{c2} , the dominant contribution to the diamagnetism is from the very lowest modes, which are diverging there, and these lowest modes have the longest-wavelength spatial variation. On the other hand, far from T_{c2} , a great number of modes with much shorter wavelength make contributions comparable with the lowest ones, and the breakdown of the GL approximation is more severe. Because our sensitive measurements allow M' to be followed out to $2T_c$ and to high fields, and because they are obtained with rather ideal bulk samples, our data should allow quite a critical test for theoretical treatments which go beyond the region near the critical point.

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⁸It is interesting to note that the PAW curve agrees quite well with the data if the horizontal scale is expanded by a factor of 2; i.e., if (H/H_s) were replaced by $(H/H_s)^{1/2}$ in their results. Although this observation may well give guidance on how to improve their model, no rationale for such a change is presently available.

⁹For the pure materials, where $l \gg \xi_0$, H_s depends only on ξ_0 . This parameter was evaluated using the standards results $\xi(T) = 0.74\xi_0(1-T/T_c)^{-1/2}$ and $H_{c2}(T) = \Phi_0/2\pi\xi^2(T)$. These give the relation $T_c dH_{c2}/dT|_{T_c} = \Phi_0/2\pi(0.74)^2\xi_0^2$, from which ξ_0 can be determined using the known values of dH_{c2}/dT and T_c . For the alloy, H_s is calculated by multiplying the value of H_s computed for pure lead by the factor $(1 + \xi_0/l)^2$. The required ratio of ξ_0/l can be determined from the relation $(T_c dH_{c2}/dT)_{Pb}/(T_c dH_{c2}/dT)_{PbTi} = \chi(\alpha)$, where $\chi(\alpha)$ is a known function [see Ref. 5, p. 338] of ξ_0/l . These procedures yield $\xi_0(\text{In}) = 3640 \text{ \AA}$, $\xi_0(\text{Pb}) = 870 \text{ \AA}$, and $\xi_0/l = 3.12$ for the alloy, and the values of H_s shown in Table I.

Hypersound Attenuation in Superconductors by Quasiparticle Creation*

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The attenuation of 10-GHz longitudinal sound waves in superconducting molybdenum ($T_c = 0.914 \text{ K}$) and cadmium ($T_c = 0.500 \text{ K}$) shows the high-frequency behavior predicted by the BCS theory. In particular, the onset of the rapid drop in attenuation with decreasing temperature that is characteristic of superconductors is shifted downward to the temperature T_v (0.905 K in molybdenum and 0.490 K in cadmium) at which the superconducting energy gap equals the phonon energy. The analysis of the measurements indicates a large anisotropy in the energy gaps of both metals.

In the original publication of the BCS theory of superconductivity,¹ the low-frequency limit (i.e., phonon energy $h\nu$ small compared with the energy gap 2Δ) for the attenuation of sound was written as

$$\alpha_S/\alpha_N = 2f(\Delta), \quad (1)$$

where α_S and α_N are the acoustic attenuations in the superconducting and normal states, and f is the Fermi function. For higher frequencies the results include contributions to the phonon absorption not

only from thermally excited quasiparticles [the sole contributor in Eq. (1)], but also from the creation of pairs of quasiparticles which can occur above the temperature T_ν at which the phonon energy just equals the energy gap. The general expression for the attenuation is²

$$\alpha_S/\alpha_N = 2 \int_{\Delta}^{\infty} (1 - \Delta^2/EE')(EE')[(E^2 - \Delta^2)(E'^2 - \Delta^2)]^{-1/2} [f(E) - f(E')] dE \\ + \int_{\Delta - h\nu}^{\Delta} (1 - \Delta^2/EE')(EE')[(E^2 - \Delta^2)(E'^2 - \Delta^2)]^{-1/2} [f(E) - f(E')] dE, \quad (2)$$

where $E' = E + h\nu$ and the last term on the right occurs only above T_ν . In Fig. 1 we show the temperature dependence of α_S/α_N calculated from Eq. (2) at several frequencies using the BCS temperature variation of the energy gap parameter Δ . The last integral on the right-hand side of Eq. (2) is responsible for the discontinuous jump in attenuation ratio that occurs at T_ν , and the subsequent decrease to 1.0 as the temperature T approaches the transition temperature T_c . Since the slow variation in attenuation between T_ν and T_c can only be observed for relative frequencies higher than any that have been used to date, we limit our discussion to the observations of the difference between T_ν and T_c , and the discontinuous (or at least very steep) drop in attenuation just below T_ν .

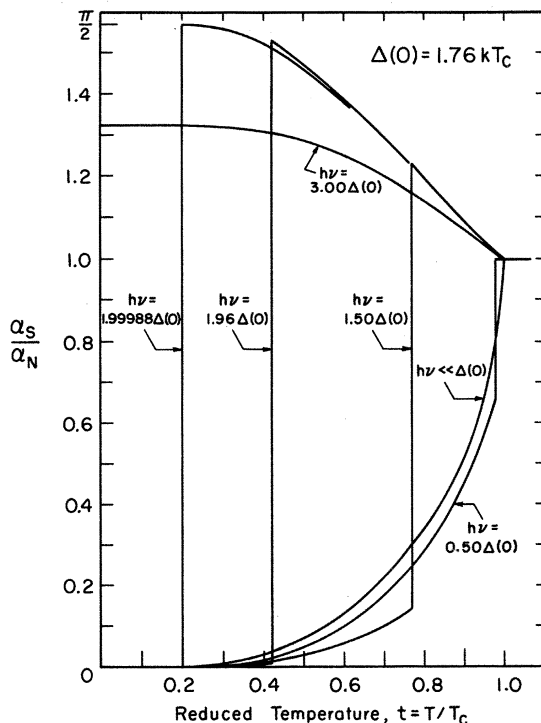


FIG. 1. Ultrasonic attenuation ratio as a function of temperature for several frequencies as calculated from the BCS theory of superconductivity. Note that all reported experimental work to date is in the frequency region bounded by the curves for $h\nu = 0.50\Delta(0)$ and $h\nu \ll \Delta(0)$.

All previously reported measurements of acoustic attenuation in superconductors are in the low-frequency limit with the following exceptions: aluminum ($T_c = 1.175$ K) at 9.3 GHz by Fagen and Garfunkel³; a preliminary report of the molybdenum work presented here⁴; and some recent work on aluminum at 9.2 GHz and iridium ($T_c = 0.102$ K) at 0.75 GHz by Dobbs et al.⁵ All of the work on aluminum^{3,5} and iridium⁵ were at such a low relative frequency [$h\nu/\Delta(0) < 0.25$] that the observation of a difference in temperature, $T_c - T_\nu > 0$, was at the limit of detectability. In the present work we report on the acoustic attenuation of molybdenum⁴ at 9.4 GHz [$h\nu/\Delta(0) = 0.32$], and for cadmium at 9.3 GHz [$h\nu/\Delta(0) = 0.50$].⁶

The experimental technique was essentially the same as that described by Fagen and Garfunkel.³ The samples, pure single crystals, were formed as thin disks with principal directions normal to the surface {the (111) direction was 4° from the normal to the molybdenum surface, and the [0001] direction was less than 1° from the normal to the cadmium surface}. The samples were bonded between two cylindrical quartz rods and cooled by thermal contact with a He³ bath which could be cooled to 0.35 K. The other ends of the quartz rods were inserted in microwave cavities and arranged so that hypersound was generated in one cavity and detected in the other (see description by Fagen and Garfunkel³). Relative attenuation measurements were made, comparing the attenuation above T_c with that at any temperature below. For the zero magnetic field measurements, the geomagnetic field was canceled to less than 0.007 G.

Two different procedures were used for determining T_c . In the case of molybdenum, T_c was measured on the sample in a separate apparatus by the rapid change in penetration depth that occurs at T_c at 1 MHz [see Fig. 2(a)]. It was found to be 0.9138 K.⁷ In the case of cadmium, T_c was obtained by extrapolating the critical magnetic field of the sample, H_c , to zero [see Fig. 3(a)]. The critical magnetic field was found, in place, by determining that value of field at which the acoustic attenuation jumped to the normal-state

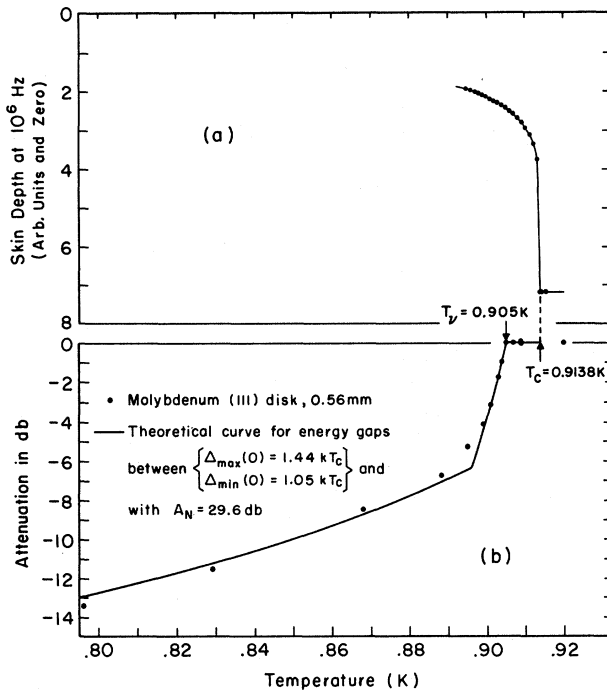


FIG. 2. Temperature dependence of experimental results for molybdenum: (a) the skin depth at 10^6 Hz, which gives $T_c = 0.9138$ K; (b) ultrasonic attenuation at 9.4 GHz, which gives $T_v = 0.905$ K. The theoretical curve was calculated using these values of T_c and T_v and finding a satisfactory fit to the data by using a range of energy gaps (see text). An error in $T_c - T_v$ can cause comparable error in the range of energy gaps needed.

value (obviously measurements could only be made for $T < T_v$). The curves for determining the critical field showed a negligible hysteresis and were very sharp since the sample-field geometry gave a very small demagnetization factor (the magnetic field was parallel to the thin disk). The transition temperature for cadmium was found to be 0.500 K.⁷

The results of the absorption measurements are shown as the points plotted in Figs. 2(b) and 3(b). The solid lines were calculated as will be described below. From a comparison of the (a) and (b) parts of both sets of data it is clear that $T_c - T_v \sim 0.010$ K > 0 . We also note that the discontinuity predicted by the BCS theory (Fig. 1) is absent in both Figs. 2(b) and 3(b). However, the discontinuity is a feature of the single, isotropic energy gap of the BCS theory; and since we believe that there is energy-gap anisotropy in pure, crystalline superconductors, we should expect that the discontinuities of Fig. 1 would spread out into a rapid, but continuous, change. This is precisely the case in both Figs. 2(b) and

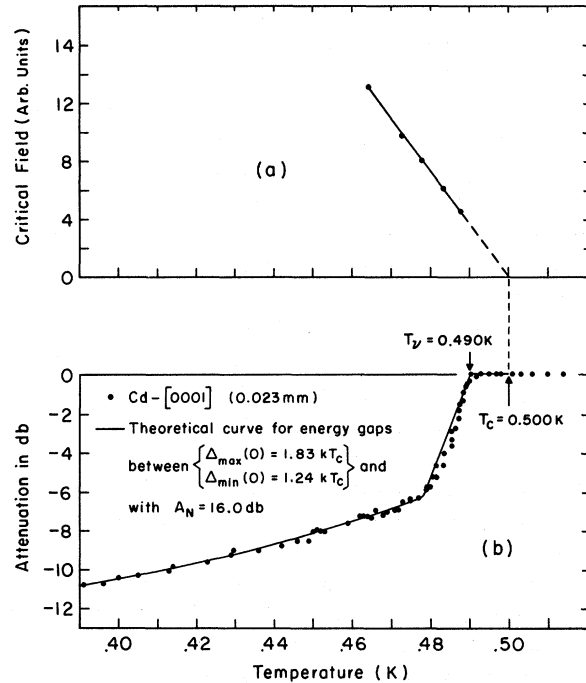


FIG. 3. Temperature dependence of experimental results for cadmium: (a) the critical magnetic field, which gives $T_c = 0.500$ K; (b) ultrasonic attenuation at 9.3 GHz, which gives $T_v = 0.490$ K. These values of T_c and T_v are used in calculating the "best"-fit theoretical curve. An error in $T_c - T_v$ of the order of 0.001 K (our estimated error) would cause a shift of 5% in the range of energy gaps to fit the data.

3(b), and along with the finite difference, $T_c - T_v$, demonstrates the important features of the theoretical predictions.

The actual fit of the data, shown by the solid curves, was made by assuming that the attenuation is the sum of attenuations for a range of energy gaps with a uniform weighting. The temperature dependence for each gap was assumed to be that of the BCS theory and the normal-state attenuation was selected so that the calculated curve goes through the lowest temperature points. We then picked the range of energy gaps to "best" fit the data using a computer evaluation of the integrals of Eq. (2), giving equal weights to the contribution of the gaps in the selected range. The point on each curve marked T_v is well defined and gives us the largest gap (assuming the BCS temperature variation of the gap). The smallest gap is not so accurately determined since the break in slope at the low-temperature end of the steep section is not as accurately determined as that at T_v . The range of values of $\Delta(0)$ for molybdenum [in the (111) plane] is from

$1.05kT_c$ to $1.44kT_c$. For cadmium it is from $1.24kT_c$ to $1.83kT_c$. Clearly, an error in determining $T_c - T_v$ leads to an error in the estimated energy gap, possibly amounting to as much as 15% for molybdenum and 7% for cadmium.

In conclusion, the experiments reported here confirm, at least qualitatively, the predictions of the BCS theory^{1,2} regarding high-frequency sound absorption in superconductors, if one takes into account anisotropy of the energy gap. Furthermore, the method gives a measure of the energy gap (rather, the range of energy gaps) on the part of the Fermi surface normal to the propagation direction. Finally, we note that we appear to observe an unusually large anisotropy for such high-symmetry planes. This may be a consequence of the oversimplification of our model.

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⁷The 1962 He³ temperature scale: R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Nat. Bur. Stand., Sect. A **68**, 579 (1964).

LO-Phonon-Assisted Two-Phonon Absorption in KI†

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The two-photon absorption constant is measured experimentally with high resolution in the exciton region of KI. Fine structure is resolved in which the 2P exciton is seen at 6.263 eV. The peak at 6.285 eV is identified as a LO-phonon-assisted transition. The latter assertion is verified theoretically by invoking third-order time-dependent perturbation theory.

Recently, much interest has been generated in the exciton-phonon interaction in alkali halides. Under high resolution, excitons exhibit fine structure which Baldini, Bosacchi, and Bosacchi¹ have claimed to be due to both linear and quadratic exciton-phonon interactions. Earlier, in the original two-photon absorption experiment of Hopfield, Worlock, and Park,² weak structure was seen in KI around the 2P position. A probable cause of this was attributed by them to be

degenerate valence-band splitting. It was this controversy that initiated the present two-photon work at a much higher resolution than the earlier one. The refinements in experimental techniques which allowed us to measure the fine structure of KI will be presented in a later paper.

The crystal was probed with two beams of plane-polarized light at approximately 6°K. The polarization vectors were mutually parallel to the (001) axis, and the beams were incident