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This Letter reports the observation in several CdS crystals of an acoustic wave propagating with anomalously slow velocity under acoustic gain conditions. In a pulsed ultrasonic transmission experiment, this is manifested by the appearance of additional pulses at the output transducer. These observations were made at room temperature at 10, 15, 20, 30, and 60 Mc/sec. It is suggested that these observations may be explained as a collective propagation of momentum by the phonon field much like the phonon-gas description of second sound.¹

VOLUME 11, NUMBER 6

The experimental configuration was similar to that described by Hutson, McFee, and White,² consisting of a CdS crystal sandwiched between two fused quartz rods. Shear waves polarized along the *c* axis of CdS were propagated through this configuration; the direction of propagation was perpendicular to the *c* axis of the CdS. The polished CdS and quartz interfaces were bonded with indium. The CdS crystals³ were insulating in the dark and under conditions of illumination used the resistivity was 10^4 to $10^5 \Omega$ -cm. All CdS crystals which showed this phenomenon had maxi-



FIG. 1. Normal sound propagation in CdS in the dark. The upper trace shows the rf input pulse (15 Mc/sec). The lower trace shows the sound pulses received at the opposite end of the configuration described in the text. Time runs right to left; the time scale is 4 μ sec/cm. The transit times of the sound wave through each quartz rod and this CdS crystal are 6.8 and 5.3 μ sec, respectively. Pulse 1: Sound transmitted straight through configuration. Pulse 2: Echo in CdS. Pulse 3: Echoes in quartz rods.

mum acoustic gains $\geq 40 \text{ dB/cm}$ for 20-Mc/sec ultrasonic waves.

Figure 1 shows oscilloscope traces of the transmitted and received sound pulses when the crystal was in the dark. Figure 2 shows the behavior under acoustic gain conditions with large-amplitude (approximately $0.1-W/cm^2$) input sound pulses injected into the CdS. A trailing pulse, not present in the dark, is observed to arrive 2.5 μ sec after the first. The trailing pulse was identified as being almost completely a shear wave of the same polarization as the injected sound wave. That sound pulse which corresponds to an echo within the CdS is not visible in Fig. 2 because the voltage pulse was not on long enough to amplify the wave on its final traversal through the CdS. If longer voltage pulses are applied, echoes of the ordinary sound pulse within the CdS and additional anomalous pulses are observed. Every anomalous pulse trails an echo of the ordinary sound pulse by exactly the same time interval as the delay between the initial pulse and its trailing mate. These observations are consistent with the hypothesis that the trailing pulse is lost on each return (attenuating) trip across the CdS and that a trailing pulse is regenerated simultaneously with the reflection of the ordinary pulse from the interface between the CdS and the input quartz



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FIG. 2. Anomalous sound propagation under gain conditions in the same CdS crystal as used in Fig. 1. The main pulse has been amplified 20 dB over its dark level by application of an electric field of 1500 V/cm. Pulse 1: Sound transmitted straight through configuration. Pulse A: Anomalous trailing pulse. Pulse 3 and B: Echoes in quartz rod of pulses 1 and A. rod. When the input sound pulse was turned off, the trailing mate also disappeared indicating that this trailing pulse was not the spontaneously generated sound described in references 2 and by $McFee.^4$

The delay between the first and second pulses is accomplished entirely within the CdS since (1) the delay was the same, even when the output fused quartz rod was not used; i.e., when the output transducer was bonded directly to the CdS; (2) echoes of the main and trailing pulses in the output fused quartz rod showed that the speed of these two pulses is the same in the quartz; (3) in order to detect the trailing pulse, the amplifying voltage had to be applied for a time interval consistent with the apparent longer transit time of the trailing pulse through the CdS.

The amplitude of the second pulse was voltage dependent, extremely light sensitive, and in nonlinear relationship to the amplitude of the first pulse. Cooling the crystal caused the trailing pulse to be severely attenuated. At about 200°K, the trailing pulse had completely disppeared in all crystals. When the crystals were reheated to room temperature, the trailing pulse reappeared.

One crystal which showed this effect was shortened and still exhibited the trailing-pulse phenomenon. The delay between the main and trailing pulses was reduced in proportion to the shorter length. It has not yet been possible to obtain crystals much longer than 1 cm which have the appropriate properties necessary to exhibit this phenomenon.

Since the smallest dimension transverse to the direction of propagation was larger than the active dimension of the transducers, which in turn was 50 to 100 times the wavelength of the sound, it is not reasonable to ascribe the second-pulse phenomenon to diffraction effects. The transverse nature of the wave would also rule out the more usual "trailing-pulse" phenomenon described by Redwood.⁵

Attempts to detect sound reflections and surface modes off the transverse sides of the crystal proved unsuccessful, as did all attempts to demonstrate that the trailing pulse could be associated with either "ringing" of transducers, mode conversions of ordinary sound waves, or the electronics. Thus, the trailing pulse can be most easily interpreted as a slower transmission of phonon energy through the CdS.

The apparent slow velocity increased at lower temperatures. The room-temperature velocity varied by about 20% among crystals of the same

length. The slowest room-temperature velocity measured was $v_S/1.6$. Here, v_S is the velocity of the slowest mode of ordinary sound which propagates in the basal plane of CdS, and this is the only mode coupled to the gain mechanism in such a direction.

The possibility of propagating collective oscillations in the phonon field of a crystal has been previously examined by one of the authors.⁶ The analysis indicated that a collective propagation in the phonon system could exist if (1) the crystal momentum loss due to umklapp collisions were small enough, and (2) the mixing or normal collisions were fast enough. At some low temperature both of these conditions might be fulfilled in insulating crystals. The velocity of the collective mode would be

$$V_{II} = \gamma v_s$$

where v_s is the velocity of first sound and γ is $3^{-1/2}$ for a spherically symmetric phonon distribution.

Further theoretical analysis shows that even at higher temperatures such a wave could propagate if an appropriate gain mechanism were available to phonons. The gain mechanism would both overcome crystal momentum losses, thus allowing condition (1) to be satisfied, and increase the normal collision rate, and thus help condition (2) to be met.

The gain mechanism appropriate to piezoelectrically active modes in CdS at room temperature is the greatly increased phonon emission by the electrons when their drift velocity exceeds the velocity of sound. This increased emission rate has been discussed by Pippard⁷ in the quantum limit and by White⁸ in the classical limit. Theoretical analysis shows that the bulk of the emission occurs in a band of phonon frequencies below 10^{11} cps and that the gain would be sufficient to overcome relaxation times shorter than 10^{-8} sec. Phonons of these frequencies are loosely coupled to the major part of the crystal specific heat as pointed out by Herring,⁹ and their dark relaxation time for crystals of this purity may well be as long as 10⁻⁸ sec.

The normal phonon collisions which are necessary to maintain the collective nature of the anomalous wave throughout the CdS crystal are probably higher order electron-phonon collisions. These collisions would tend to keep the crystal momentum within the active phonon band, as (a) the piezoelectrically active mode would have the fastest collision rate, and (b) the electrons are VOLUME 11, NUMBER 6

not able to couple strongly to the high-frequency phonon modes because of energy and momentum conservation considerations. The normal phonon collisions not involving electrons (relating to the dark relaxation rate) do, of course, couple to thermal phonons and are the dominant damping collisions for the collective wave. The enhanced low-temperature damping of the trailing pulse could be explained by the increase in second viscosity¹⁰ due to a slowing down of the normal collision rate within the active band, below that rate needed to maintain the collective wave.

Since the collective wave can propagate only in a direction which permits acoustic gain, the fact that the trailing pulse has never been observed to propagate in the attenuating direction is also explained by the collective phonon wave hypothesis. Because the gain mechanism and the mixing collisions act selectively on phonons of a particular mode, one would expect this mode to dominate the collective wave whose velocity would then be approximately this mode's velocity times γ . The value of γ will be larger than $1/\sqrt{3}$ for the phonon distribution obtained under amplification conditions, which is peaked in the direction of carrier flow.

It is suggested that the collective mode is excited and detected in the In-CdS interfaces at the input and output ends of the crystal. The incident sound wave (say 10 Mc/sec) enters the spacecharge region of the interface, where the electron drift velocity is $< v_s$, and generates a piezoelectric field. The electron density responds rapidly to this field, and the modified charge density modulates the electron-phonon collision process producing a phonon density varying at 10 Mc/sec. The collective mode thus appears as an

amplitude-modulated group of phonons which is amplified in the bulk of the crystal. At the output end of the crystal the charge density in the spacecharge region is modulated through electron-phonon collisions with the collective mode, generating a coherent piezoelectric strain at the 10-Mc/sec rate; the resulting sound wave is then detected by the output transducer. Cancellation in the generation and detection of the collective wave may be expected to occur for certain thicknesses of the space-charge region. Experiments indicate that the extent of diffusion of the indium into the CdS and the intensity of illumination at the interfaces are critical in determining the magnitude of this effect.

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SUPERCONDUCTIVITY OF TITANIUM

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From recent work indicating that manganese impurities have localized moments in titanium,^{1,2} it has been inferred² that T_c , the superconducting transition temperature in zero magnetic field, of very dilute Ti-Mn alloys should decrease with increasing Mn content. On the other hand, earlier results of Matthias et al.³ on Ti-Mn alloys containing Mn in excess of 1.5% extrapolated to a T_c of about 0.4°K for pure Ti

and were interpreted as evidence that, for Ti-Mn alloys containing less than 2.5% Mn, T_{c} increases monotonically with increasing Mn content.

The purpose of this note is to present some of the more significant results of a current investigation of the superconducting properties of "pure" Ti and also data obtained in the previously unexplored region of Ti-Mn alloys where



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