The present results are applicable to rare-earth metals only when in a ferromagnetic state, either naturally or under the action of a strong magnetic field.[12] For spiral antiferromagnetic structures of crystals with only one atom per unit cell, Kasuya as well as Yosida has found a spin-wave spectrum give by[11]

$$\hbar\omega_q \propto 2J[\{d-I(\mathbf{q})+I(\mathbf{q}_0)\} \times\{I(\mathbf{q})-\tfrac{1}{2}I(\mathbf{q}_0+\mathbf{q})-\tfrac{1}{2}I(\mathbf{q}_0-\mathbf{q})\}]^{\frac{1}{2}}, \quad (17)$$

where d is a constant used to describe anisotropy energy in the hard direction of magnetization, i.e., is positive, and $I(\mathbf{q})$ is directly proportional to $\sum_K[f(\mathbf{K})-f(\mathbf{K}-\mathbf{q})]$ in the present notation. $\mathbf{q}_0$ gives the pitch of the ground-state spiral structure. Formula (17) indicates that in the spin-wave spectra of antiferromagnetic structures images of the Fermi surface such as found in the ferromagnetic case will appear, and with comparable magnitudes. The condition for a kink is that the vector $\mathbf{q}$ satisfy any one of the conditions:

$$|\mathbf{q}+\mathbf{K}|=2k_F, \quad |\mathbf{q}+\mathbf{q}_0+\mathbf{K}|=2k_F, \quad |\mathbf{q}-\mathbf{q}_0+\mathbf{K}|=2k_F, \quad (18)$$

where $\mathbf{K}$ is again any one of the reciprocal lattice vectors.

In conclusion, a few remarks about the effect of the finite size of the ion core are in order. These are extremely difficult to treat quantitatively. However, it should be noted that to some extent these effects are allowed for in the determination of the constant G from observed resistivities, and that the dimensionless parameter that measures the importance of these effects, namely $k_F r_0$, where r_0 is the "radius" of the ion cores, has a value of 0.4. It is, therefore, not to be expected that the estimate of the relative size of the kinks given here is significantly in error.

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Photosensitive-Ultrasonic Properties of Cadmium Sulfide

HARMON D. NINE
General Motors Research Laboratories, Warren, Michigan

AND

ROHN TRUELL*
Brown University, Providence, Rhode Island

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Ultrasonic attenuation in single crystals of CdS has been observed to be a function of light irradiation. Two distinct types of behavior have been observed. Some crystals (type A) show a decrease of attenuation with white light application, and others (type B) show an increase of attenuation with white light. The ultrasonic attenuation and the conductance of the crystals were measured as a function of temperature. An excellent correlation between the conductance and the ultrasonic attenuation is evident for type B crystals. A strong correlation between the directional piezoelectric properties of CdS and the ultrasonic attenuation in both types of CdS is also shown. An interaction between conduction electrons and stress waves coupled by the piezoelectric property of CdS is isolated as the dominant mechanism for the photosensitive ultrasonic attenuation in CdS of type B. Two or more competing effects appear to be responsible for the type A photosensitive attenuation behavior.

INTRODUCTION

IN a previous paper by one of the authors it has been observed that there are pronounced changes in the ultrasonic attenuation in single-crystal samples of CdS when such samples are exposed to light over the spectral range from the band edge at 5100 to 8000 A.[1] In that paper, two distinct effects of light irradiation on the ultrasonic attenuation in different CdS crystals, called type A and type B crystals, were discussed. Type A crystals showed a decrease of attenuation upon irradiation with light in the indicated spectral region and type B crystals showed an increase in attenuation upon irradiation. This paper describes recently completed work by the authors on the temperature variation of both ultrasonic attenuation and electrical conductance and further work on the photosensitive attenuation as a function of crystal direction which has made it possible to isolate the mechanism primarily responsible

* Some of the low-temperature measurements on cadmium sulfide were made at Brown University and in this connection acknowledgement of support is made to the National Science Foundation.

[1] H. D. Nine, Phys. Rev. Letters 4, 359 (1960).

for the phenomena observed. A pulse-echo technique was used to make the ultrasonic measurements.[2]

The CdS crystals were grown by a vaporization-recrystallization process.[3] The crystals are "pure" in the sense that they are not deliberately doped. They, however, contain both impurity and stoichiometric defect structure which introduce defect levels into the band gap. These CdS crystals are highly photoconducting in the wavelength region from 5100 to 8000 A and can be quenched by infrared irradiation (most effective at 9000 A). A detailed description of the photoresponse of attenuation and conductance to light wavelength and a description of the physical properties of the samples is contained in reference 1.

Light-sensitive effects on the elasto-mechanical characteristics of CdS have also been reported by Gobrecht and Bartschat.[4] Their observations were made by loosely coupling a CdS single-crystal plate to a high-frequency, vacuum-tube oscillator of variable frequency and utilizing the piezoelectric property of CdS to drive the CdS crystal at the frequency of the vacuum-tube oscillator.[5] These investigators observed qualitative effects of temperature and infrared irradiation on the piezoelectric and elasto-mechanical properties of CdS—effects which in this paper are called type B behavior.

The pulse-echo method of measurement used by the present authors allows a quantitative measurement of the changes in damping (i.e., attenuation changes) not possible by the oscillator method. In addition, by use of an external transducer which may be used in the pulse-echo technique, it is possible to distinguish more easily between changes which are only amplitude changes of the observed acoustical waves (or oscillations) as compared to changes in the damping of the acoustical waves (or oscillations). Use of an external transducer also permits an investigation of the effect of both compressional and shear waves as a function of crystal direction.

Using the pulse-echo technique, measurements can be made both with an external quartz transducer coupled to the CdS crystal and with the single CdS crystal used as both sample and transducer. The self-transducer[6] use of CdS is possible because CdS is piezoelectric itself. It is important to realize that these two pulse-echo methods are different because, in the first instance, with the separate quartz transducer, a mechanical wave is introduced into the sample and the effects are those resulting only from a mechanical wave. Additional complexity in interpretation of the effects is introduced in the second instance where an applied oscillating electric field is placed across the sample in addition to the mechanical wave (or waves) generated by this electric field. Changes in the applied electric field, such as reduction of the field by photoactivated electrons, can produce amplitude changes in the mechanical wave; they cannot, however, produce attenuation changes unless a nonlinear behavior is present.

The self-transducer use of the CdS crystals is somewhat like the oscillator use of CdS made by Gobrecht and Bartschat. However, when used as a self-transducer, the surfaces of the large single crystals of CdS act as transducers as discussed in reference 6; while in the oscillator use of CdS, the single-crystal plates oscillate as a whole. In both the oscillator and self-transducer methods the foregoing discussion on electrically caused amplitude changes applies. However, using the pulse-echo self-transducer technique, quantitative measurements of the ultrasonic attenuation changes can be made.

The more quantitative nature of observations possible using the pulse-echo technique and the use of a separate transducer allows a better assessment of the possible causes of the photosensitive piezoelectric and elasto-mechanical properties of CdS to be made.

EXPERIMENTAL RESULTS

The two types of behavior, type A and type B, which the authors have observed, represent two extremes of behavior. In different crystals there are found intermediate magnitudes of these effects between the extremes of type A and type B. The maximum in attenuation as a function of light intensity reported by Hutson[7] was not observed in the extreme types A and B. A maximum was seen in one intermediate crystal which shows type B behavior with low-intensity light irradiation but goes through an attenuation maximum as light intensity increases and shows type A behavior with more intense light.

The ultrasonic attenuation has been studied over a temperature range from 2°K to room temperature. Ultrasonic velocity changes accompanying these attenuation effects have also been measured. The application of magnetic fields up to 15 000 gauss produces no detectable effect on the ultrasonic results at room temperature.

Except as specifically noted, both the separate transducer and the self-transducer methods of measurement give the same results and measurements were made both ways. The data displayed in the figure showing temperature variation of ultrasonic attenuation were obtained using the self-transducer method since it eliminates the external transducer bonding problem which often causes trouble at low temperatures.

The work reported in reference 1 showed a correlation between the electrical conduction and the ultrasonic attenuation and suggested an electron-acoustical inter-

[2] B. Chick, G. Anderson, and R. Truell, J. Acoust. Soc. Am. **32**, 186 (1960).
[3] D. R. Boyd and Y. T. Sihvonen, J. Appl. Phys. **30**, 176 (1959).
[4] H. Gobrecht and A. Bartschat, Z. Physik **153**, 529 (1959).
[5] The experimental arrangement is described in H. Gobrecht and A. Bartschat, Z. Physik **136**, 224 (1953).
[6] A discussion of "Production of sound in piezoelectric crystals" may be found in E. H. Jacobson, J. Acoust. Soc. Am. **32**, 949 (1960).
[7] A. R. Hutson, Phys. Rev. Letters 4, 505 (1960).

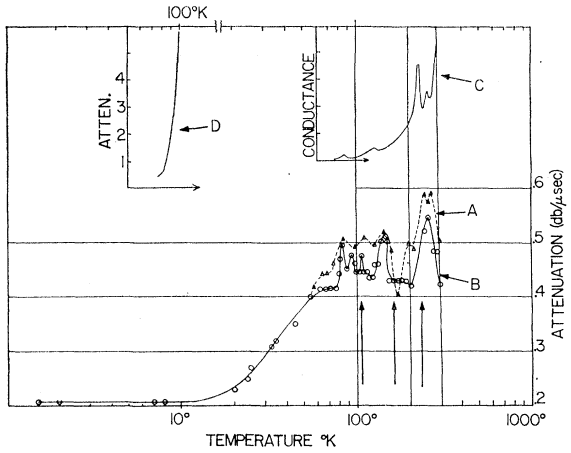

FIG. 1. Temperature dependence of attenuation in CdS using sample as self-transducer. A: Attenuation-temperature curve of type B crystal for descending temperature and dark condition. B: Attenuation-temperature curve for rising temperature after irradiation with visible light at 70°K for comparison to thermally-stimulated current curves. Arrows indicate peaks in thermally-stimulated current curve found by Bube. C: Conductance-temperature curve measured during descending temperature run. Measured along with curve A. Conductance on arbitrary scale. D: Attenuation-temperature curve for type B crystal under intense irradiation by visible light.

action. A group of experiments was undertaken to further test the correlation between the electrical conduction and the acoustical response of the CdS crystals. The detailed characteristics exhibited by the two types of crystals found by these experiments are as listed below.

Type B

1. No differences in the light-sensitive effects were observed for type B behavior between using a separate transducer and using the CdS as a self-transducer for type B behavior.

2. A large increase in attenuation is observed in going from dark to light condition for light in the wavelength range 5100 to 8000 A. The magnitude of the attenuation change at room temperature is from approximately 0.4 db/μsec dark to >4 db/μsec light and is too large to be measured (limit of measurability is 4 db/μsec) with intense light, incident on the sample at room temperature. The wave appears to be completely damped out by a sufficiently intense light source. On removing all the incident light, the attenuation returns rapidly to the original dark value (at room temperature). The sample shows a large photoconductance response.

3. The incidence of infrared light (8000 to 10 000 A) causes the crystal, which has been or is being illuminated with white light, to recover its original, lower, or dark attenuation value. Infrared irradiation of the CdS crystal also increases markedly the rate of recovery of attenuation to the original dark value compared to removing all incident radiation. Infrared light quenches the photoconductance.

4. Since quantitative measurements of attenuation could be made, it was possible to plot attenuation versus temperature data for comparison to conductance versus temperature data. As the temperature is decreased from room temperature, the dark value of the attenuation decreases slowly and shows structure down as far as 60°K (Fig. 1A). The electrical conductivity was measured (Fig. 1C) together with the attenuation and the major peaks of the attenuation measurements correlate with those of the conductivity measurements. In addition, the ultrasonic attenuation was measured as a function of increasing temperature (Fig. 1B). At 70°K, during an increasing temperature run, the sample was irradiated with light from a tungsten-filament lamp for the purpose of comparing the positions of the attenuation peaks with the positions of the peaks obtained from the standard type "thermally stimulated current" results of conductivity measurements such as those of Bube.[8] The attenuation-temperature curve peaks do seem to agree in position with those from the conductivity measurements of Bube. More structure appears in the attenuation data than in the conductivity data. The amplitudes of the various peaks in the attenuation-temperature data depend strongly on the light-excitation history of the sample.

The response time of the attenuation as the temperature changes is more rapid than is the corresponding response time for the conductivity measurement.[9]

5. The time rate of change of attenuation from dark to light values, or during recovery, decreases as the temperature is lowered until, at 40°–60°K, the change occurs so slowly that it is almost undetectable. The rate of response of the photoconductance is also slowed by low temperatures.

6. The attenuation change from dark to light, measured as a function of decreasing temperature, becomes smaller in magnitude as the temperature is lowered. Measurements taken with intense illumination show unmeasurably high attenuation values and low amplitude at room temperature; but at temperatures below 100°K, the attenuation becomes measurable. (See Fig. 1D). The photoconductive response is also smaller in magnitude.

7. Measurements of ultrasonic velocity changes accompanying the attenuation increase from dark to light condition showed, at room temperature, a decrease in velocity of 0.5% with the most intense light used.

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[8] R. H. Bube, Phys. Rev. **92**, 1105 (1955).

[9] In addition to the low-temperature behavior reported here using the self-transducer method, the attenuation-temperature behavior has been examined with type B crystals up to 600°C. At about 470°C, the attenuation became so large that compressional wave measurements were no longer possible. By increasing the temperature still further, it was found that a new shear-wave mode appeared, and this mode was present at temperatures up to at least 600°C. This type of attenuation behavior may indicate a phase transformation as it does, for example, in quartz at 575°C. However, there is not a known phase transformation in CdS at normal pressure for this temperature range.

Type A

1. Measurements were again made both with an external quartz transducer coupled to the CdS crystal and with the CdS sample used as its own transducer. In this case, differences are observed in both amplitude and attenuation between these two methods of measurement. For example, with a quartz transducer on the CdS sample it is observed that, from dark to light condition, the attenuation always decreases and the amplitude always increases. On the other hand, when the CdS sample is used as its own transducer, there are two effects—the attenuation decreases at low-pulse amplitude in going from dark to light conditions (low gain) and the effect tends to reverse so that the attenuation actually increases when the pulse amplitude (gain) is increased sufficiently. This last effect appears to depend on the pulse amplitude which indicates that a nonlinear or strain-amplitude-dependent effect is present. The same effect may be present in the case of type B performance, but it has not been observed in that case; the reason for the difficulty in determining whether or not this effect is present is simply that the attenuation in the dark-to-light transition goes beyond attenuation values that can be measured. Where differences occur between the external-transducer results and the self-transducer result, the external-transducer results are regarded as more reliable.

2. Using an external transducer, type A samples show a decrease in attenuation from dark to light condition for light in the wavelength range 5100 to 8000 A. The decrease in attenuation is about 50% for the largest attenuation change (of this type) observed. A large photoconductance is observed.

3. Infrared irradiation is not as effective in restoring the attenuation to its original value under dark conditions as it is with type B samples. The infrared light does, however, effect a partial recovery. Infrared quenches the photoconductance to the dark value.

4. Using the CdS as a self-transducer, as the temperature is lowered, the dark value of attenuation increases as shown in Fig. 2. As the attenuation becomes too large to be measured, at about 125°K, a shear wave arises and grows in amplitude as the temperature is decreased; at the same time, the attenuation of this shear mode decreases as the temperature decreases.

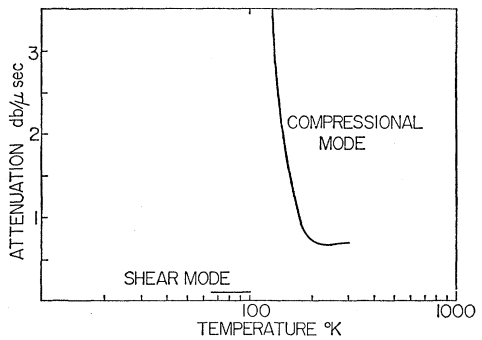

FIG. 2. Attenuation-temperature curve for type A crystals using sample as self-transducer.

Using an external transducer, the measurement of the dark value of the attenuation shows the same trend with temperature as the self-transducer measurement. Temperature effects in the acoustical bond between the external transducer and the CdS crystal do not allow reliable measurements to be made below about 150°K. The conductance of sample A falls off much like sample B.

5. A time rate of change in attenuation could not be studied as with type B behavior because, as can be seen from Fig. 2, the temperature range in which the effect should be most pronounced is not accessible (attenuation-wise) in type A experiments. The rate of photoconductive response is slowed as with type B.

6. Measurement of attenuation as a function of decreasing temperature with the sample illuminated shifts the curve slightly toward lower temperatures. The photoconductance becomes less as temperature decreases.

7. Measurements of the largest velocity change observed, accompanying the attenuation decrease, in going from dark to light conditions, showed a very small velocity decrease of about 0.04%.

The excellent correlation between the electrical conductance and ultrasonic attenuation of the type B crystals indicates a mechanism connecting the two effects.

Evidence is very strong, if not conclusive, that the dominant factor in determining the observed attenuation behavior is a consequence of the piezoelectric properties of CdS. This can be shown from a comparison of the observed attenuation effects with the piezoelectric polarization effects to be expected. CdS crystals have hexagonal structure and belong to the *6mm* crystal class. Ultrasonic stress waves propagated along the various crystal axes produce polarizations P_i as specified by the relation

$$P_i = d_{ijk}\sigma_{jk},$$

where σ_{jk} are the stress components.

For CdS with *6mm* symmetry, the nonzero matrix values of the piezoelectric moduli d_{ijk} are d_{311}, d_{322}, d_{333}, d_{223}, d_{232}, d_{131}, and d_{113} or, in the usual matrix notation,[10]

	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
P_1	0	0	0	0	d_{15}	0
P_2	00	0	0	d_{24}	0	0
P_3	d_{31}	d_{32}	d_{33}	0	0	0

From Tanaka and Tanaka,[11] $d_{31}=d_{32}=4.6\times10^{-8}$ cgs units, $d_{24}=d_{15}$ (values not reported), and $d_{33}=7.7\times10^{-8}$ cgs units.

Comparison of measured, photosensitive, ultrasonic-

[10] See for example, J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, New York, 1957), p. 116.

[11] T. Tanaka and S. Tanaka, J. Phys. Soc. Japan **15**, 726 (1960).

TABLE I. A comparison of the piezoelectric polarizations induced by given ultrasonic stress waves to the photosensitive ultrasonic attenuation observed for these stress waves in cadmium sulfide samples A and B.

Stress applied							
L wave		*S* wave		Piezo-electric modulus	Polarization	Photosensitive response	
c axis	⊥ to *c* axis	*c* axis	⊥ to *c* axis			A	B
	σ_{11}			d_{31}	P_3	NME[a]	Small
	σ_{22}			d_{32}	P_3	NME	Small
σ_{33}				d_{33}	P_3	Medium	Large
		σ_{23}		d_{24}	P_2	Weak	Small
		σ_{13}		d_{15}	P_1	Weak	Small
			σ_{12}	0	None	NME	NME
			σ_{32}	d_{24}	P_2	Small	Medium
			σ_{21}	0	None	NME	NME
			σ_{13}	d_{15}	P_1	Small	Medium

[a] NME: no measurable effect.

attenuation changes, in various crystal directions, with the piezoelectric polarizations expected for stress-wave propagation in those directions shows nearly perfect correlation with the presence or absence of the measured attenuation changes.

Table I shows for the two types of crystals, and for different crystal directions, the comparison between the ultrasonic-attenuation response to light for a stress wave in a given direction and the piezoelectric response expected for the stress wave.

DISCUSSION

The correlation between the attenuation response observed and the polarization to be expected from the piezoelectric character of CdS for ultrasonic stress waves in the various crystal directions is excellent. There is also excellent agreement between the relative magnitudes of the responses and the expected relative magnitudes of the polarizations as indicated by the available values of the piezoelectric moduli. The type B crystals show complete correlation while the type A crystals fail only to show an expected response for σ_{11} and σ_{22}. The failure of the σ_{11} and σ_{22} to show a response may be attributed to the fact that the magnitudes of all the responses are much smaller in crystal A than in crystal B. Present information thus strongly indicates that the observed photosensitive ultrasonic attenuation in CdS is closely related to an interaction with the piezoelectric field.

In crystals of type B, correlation between the electric conductance and the ultrasonic attenuation shows an interaction between the electrons in the conduction band and the piezoelectric field. The observed increase in attenuation of the type B crystals can be attributed to the piezoelectric field doing work on the conduction electrons and the transfer of energy by the conduction electrons to the lattice by collisions.

With crystals of type A, there appears to be little or no correlation of the electrical conductance and the ultrasonic attenuation. However, there is good correlation between the piezoelectric effect and the ultrasonic-attenuation response. The observed attenuation effects in crystal A are much weaker and also show nonlinear character. These results have the appearance of two or more competing effects connected to the ultrasonic attenuation through the piezoelectric character of CdS.

Other sources of photosensitive ultrasonic attenuation, such as scattering from photoactivation defect sites in the lattice, are undoubtedly present; but the evidence indicates that a piezoelectric interaction is dominant in both A and B types of response.

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