FIG. 2. Dependence of the transmitted phonon drag upon intermediate layer thickness.

data, Eq. (1) yields $n_1 = n_2 \approx 10^{18}$ cm^{-3} as an average effective electron concentration in order to fit the intercept at $W_p = 0$ in Fig. 2, a not unreasonable value since Eq. (1) is based on uniform nondegenerate n layers.

The experiment of Fig. 1 represents only one of a large family of experiments which may be carried out using the transmitted phonon drag effect. For example, by applying very large electric fields in the input layer, it will be possible to produce warm or hot electrons and study the differences in phonon mean free paths as a function of electron temperature. By varying electron concentration in degenerate samples,

relevant phonon wave numbers may be varied. By applying stresses so as to alter occupancies of the valleys of the many-valley model, it should be possible to separate phonons produced by electrons having drift velocity in the small mass direction from phonons produced by drift velocity in the large mass direction. By varying the concentration of the carriers in the intermediate p layer, it should be possible to determine phonon-hole scattering cross sections quite directly for the relevant phonons. It may also be possible to study phonon transmission through insulators by applying conducting input and output coatings.

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PIEZOELECTRICITY AND CONDUCTIVITY IN ZnO AND CdS

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Zinc oxide and cadmium sulfide (hexagonal form) have been found to be vigorous piezoelectrics with electromechanical coupling constants which considerably exceed that for quartz. Both ZnO and CdS are well known as extrinsic n-type semiconductors, and in the case of ZnO the single crystals available have almost always possessed room temperature conductivities in excess of 10^{-3} ohm^{-1} cm^{-1}. A conductivity of

this magnitude effectively shorts out any macroscopic piezoelectric phenomena.

The present investigation of piezoelectricity in these compounds was undertaken to see if a piezoelectric interaction between conduction electrons and acoustical phonons could explain the large magnitude and the temperature dependence of the phonon-drag effect observed in thermoelectric-power measurements on ZnO.[1] (The

phonon-drag effect is necessarily proportional to the amount of acoustical-mode scattering.) Evidence has been presented in reference 1 and by Collins and Kleinman[2] which indicates that the inertial effective mass is only about $0.07m$ for electrons in ZnO. With this mass, deformation potential scattering could not give a coupling of the required magnitude unless the deformation potential constant were unreasonably large. Measurements of resistivity vs pressure by Hutson et al.[3] have shown that the deformation potential associated with lattice dilatation is not large.

Meijer and Polder[4] and Harrison[5] have developed a theory of piezoelectric scattering mobility for the zinc blende structure using a relaxation-time approximation. Despite differences in averaging procedures both papers derive for the mobility

$$\mu \cong 3000(m/m^*)^{3/2}(300/T)^{1/2},$$

based on a reported value of the piezoelectric constant for zinc blende of $d_{14} = -9.8 \times 10^{-8}$ statcoulomb/dyne.[6] The temperature dependence of this mobility would correctly predict the temperature dependence of phonon drag in ZnO, but a piezoelectric constant nearly an order of magnitude larger would be required. (Note that the constant obtained for zinc blende by applying pressure in the [111] direction to the ends of a bar is $d_{11}' = d_{14}/\sqrt{3} = 5.7 \times 10^{-8}$.)

In order to make piezoelectric measurements on ZnO it is necessary to quench the conductivity. This has been accomplished by compensating our n-type crystals with lithium acceptors.[7] This compensation raises the resistivity to the order of 10^{12} ohm cm at room temperature.

We have made the following sorts of piezoelectric measurements on ZnO doped with lithium: (A) Resonance-antiresonance measurements on vapor-phase grown needles, supported by nylon fibers and coupled capacitively at their ends to well-shielded micro-electrodes. (B) Direct squeeze measurements along the c axis (3 direction) of vapor-grown needles where the charge developed upon loading and unloading the crystal was captured on a large air capacitor whose voltage in turn was measured by a vibrating reed electrometer. (C) Resonance-antiresonance measurements on bars, cut from flux-grown platelets,[8] whose major faces had the c axis as their normal. (D) Resonance-antiresonance measurements on very small bars cut so that their length directions made angles of 45° and

20° with the c axis and so that the normals of the major faces were coplanar with the c axis and the length. (The lengths were only 2 to 4 mm and the transverse dimensions not ideally small since these bars had to be cut from a vapor-grown crystal.) The values of the piezoelectric d constants obtained for ZnO from these measurements are given in Table I.

Similar measurements performed on CdS crystals obtained from the Eagle-Picher Co. and annealed in sulfur vapor are reported in the Table.

It is interesting to compare the piezoelectricity in ZnO and CdS with that of quartz. The electromechanical coupling constant for an X-cut quartz plate is $k = 0.095$.[9] The comparable orientation for ZnO and CdS is a plate perpendicular to the c axis vibrating in a thickness longitudinal mode for which

$$k = (d_{33}c_{33}^E + 2d_{31}c_{31}^E)\left(\frac{4\pi}{c_{33}^D \epsilon_3^S}\right)^{1/2}.$$

Making use of the elastic constants measured for CdS [10] without regard to whether they are at constant E or constant D and scaling them up for ZnO by the factor $s_{33}(CdS)/s_{33}(ZnO)$, and dielectric constants (ϵ) of 8.2 and 9 for ZnO and CdS, respectively, we obtain $k \cong 0.4$ for ZnO and $k \cong 0.2$ for CdS.

We have adapted Meijer and Polder's[4] calculation of piezoelectric scattering to our hexagonal symmetry and find that the electron mobility as limited by piezoelectric scattering alone is, in

Table I. Piezoelectric constants (d) and the elastic modulus s_{33} for ZnO and CdS.

| | d_{33}[a] | d_{31} | d_{15} | s_{33} | |
	\multicolumn{3}{c}{$(10^{-7}$ statcoulomb/dyne)}	\multicolumn{2}{c}{$(10^{-12}$ cm²/dyne)}
ZnO	+3.6	-1.4	-3 to -4	0.83	
CdS	+3.2	-1.1	-4.3	1.35	1.60[b]

[a]The values of d have an estimated accuracy of about 10% except for d_{15} of ZnO where we would favor the larger of the two values.

[b]The second value of s_{33} for CdS was obtained from extremely weak resonances of c-axis bars and we believe it to be at constant E. Since this second value agrees with the measurement of reference 10, we believe that the conductivity of their CdS was high enough so that their measurements were at constant E.

cm^2/volt sec,

$$\mu \cong 50(m/m^*)^{3/2}(300/T)^{1/2} \text{ in ZnO}$$

and

$$\mu \cong 120(m/m^*)^{3/2}(300/T)^{1/2} \text{ in CdS.}$$

The piezoelectric scattering appears ample for the requirement of large phonon drag with a small effective mass. This calculation and these consequences will be discussed elsewhere.

Electrical conductivity in these piezoelectric materials results in a relaxation-type dispersion for the elastic constant c_{33} and also for c_{44} when propagation is perpendicular to the c axis. A theory of this dispersion has been developed and it successfully predicts the magnitude of the peak as well as the directional dependence of the photosensitive ultrasonic attenuation recently reported by Nine.[11] (K. Dransfeld of these Laboratories has observed that this attenuation does go through a maximum with light intensity.)

It also appears likely that the observations of luminescence occurring when excited (metastable) CdS is given an impact in the c-axis direction[12] have their origin in piezoelectric field ionization of shallow traps.

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PRESSURE DEPENDENCE OF CUBIC CRYSTALLINE FIELD SPLITTINGS OF S-STATE IONS[*]

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The detailed nature of the interaction between paramagnetic ions with half-filled shells (S ground states) and crystalline electric fields has been the subject of considerable discussion. The theoretical analysis of Watanabe[1] in particular has stimulated a good deal of experimental work. Recently Watanabe[2] has reviewed much of the pertinent experimental data and suggested that hydrostatic pressure might be used to clarify the problem. We had arrived at the same conclusion some time ago and had already performed such experiments prior to his suggestion. The majority of the results were presented at the Cambridge Meeting of the American Physical Society.[3] Complete reports on these and related investigations are to be submitted to the Physical Review in the near future. This note will summarize only those details which are pertinent to Watanabe's calculation.

Using apparatus similar to that previously described,[4,5] the paramagnetic resonance (PMR) spectra of Mn^{2+} and Fe^{3+} ($3d^5$, ^6S) present as trace ($\lesssim 0.01\%$) impurities in an MgO crystal have been observed as functions of hydrostatic pressure to 10 000 kg/cm^2 at room temperature. Details of these spectra and their analysis have been given by Low.[6,7] Of present interest is the cubic anisotropy energy represented by the spin-Hamiltonian term $(a/6)(S_x^4 + S_y^4 + S_z^4)$. The pressure-induced variations of the a parameters of both ions are shown in Fig. 1. Within experimental error the ratio $a_{Fe}/a_{Mn} = 10.70 \pm 0.02$ is independent of pressure. The fractional variation of a per kg/cm^2 is

$$(\partial \ln a/\partial P)_T = 4.03 \times 10^{-6} \text{ (kg/cm}^2)^{-1}. \tag{1}$$

In comparing this result with microscopic