Table I. Theoretical energies and radii of shallow surface and bulk donor states in Si.

$\|m\|$	E [a]	a [b]	E (Levine) [a]	E (Kohn) [a]
0	−11.20	63.91	−7.30	−29.0
1	−4.21	107.9	−3.24	−10.9
0	−2.00	331.7	−1.83	−8.8
1	−1.27	346.0	−1.17	−5.9
0	−0.76	866.8	−0.81	−5.7
				−2.9

[a]In units of 10^{-3} eV. [b]In units of a_0.

Y_{10}. The dipole selection rules are $\Delta m = 0, \pm 1$.

We have calculated the three lowest $m = 0$ and the two lowest $|m| = 1$ states. The $|m| \neq 0$ states are doubly degenerate.

In Table I we give our results, the energy levels calculated from Levine's work, and also those of shallow donors in the interior, as calculated by Kohn.[5] The convergence of the highest state is poorest, the highest $m = 0$ state calculated converging to about 1%. The lower states have converged to 0.1% or better. For the $m = 0$ states we took $L = 9$, and for the $|m| = 1$ states, $L = 10$ to attain this degree of convergence.

Using the expression of Petukhov, Pokrovskii, and Chaplik,[3] for the unperturbed energy, we calculate the ground-state energy to be -14.74×10^{-3} eV, and the two lowest excited states to be -6.55×10^{-3} eV. Their expressions for the perturbation energies are incorrect because of the above-mentioned error in potential. Furthermore, their first-order perturbation treatment is inadequate, particularly for excited states, as we have found that there is a substantial admixture of higher "l" states, which rapidly increases with the excited states. This admixture would be neglected in a first-order treatment.

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MULTIPLE-WAVE INTERACTIONS IN PIEZOELECTRIC SEMICONDUCTORS*

R. Mauro† and W. C. Wang
Electrical Engineering Department, Polytechnic Institute of Brooklyn, Brooklyn, New York
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This paper reports the observation of three- and four-phonon processes in cadmium sulfide. Previously, harmonic generation of ultrasonic waves in piezoelectric semiconductors and three-phonon interactions in solids have been reported.[1-4] However, to the best of the author's knowledge three-phonon processes in active media have not been observed to date, nor has there been any experimental confirmation of the four-phonon process in solids because of the extremely small signal levels involved. For the case of cadmium sulfide, however, a considerable increase in the signal-to-noise ratio is attainable due to its large effective third- and fourth-order elastic constants,[1] and because it is possible to use this material as its own amplifier.

In the usual small-signal analysis of the ultrasonic amplifier[5] the nonlinear interaction of the free carriers with the electric field accompanying the acoustic wave, as a result of the piezoelectric coupling, is neglected. In studying multiple-wave interactions this nonlinear cross term is retained resulting in the generation of new signals at the harmonics and sum and difference frequencies.[6,7]

For the observation of the three-phonon process, signals at 14 and 16 MHz were used to excite the input transducer, thereby generating two collinear acoustic waves in the CdS. Frequencies of 28, 30, and 32 MHz, some 30 dB smaller than the fundamentals, were detected at the output transducer by the heterodyning technique. The input and output transducers were resonant at 15 and 30 MHz, respectively. The difference frequency at 2 MHz was

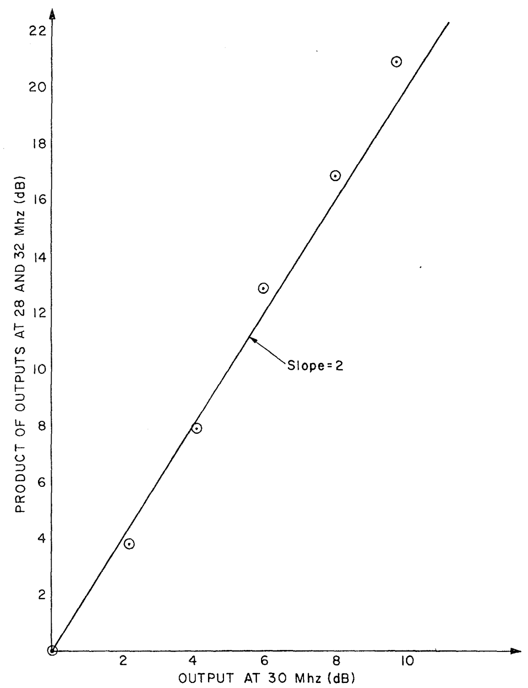

FIG. 1. Three-phonon process, product of 2nd harmonics $S_{2\omega_1}S_{2\omega_2}$ versus output-interaction term $S_{\omega_1+\omega_2}$.

detected by replacing the 30-MHz output transducer with one resonant at the difference frequency, and was observed to be more than 30 dB smaller than the fundamentals.

To explain this three-wave interaction, let the fundamental electric field $E(x,t)$ be of of the form $E_{\omega_1}e^{j(k_1x-\omega_1t)}+E_{\omega_2}e^{j(k_2x-\omega_2t)}$ with similar expressions for the strain $S(x,t)$ and the carrier density $n(x,t)$. Retention of the nonlinear cross term modifies the current density equation $J=\sigma E+D_n(\partial n/\partial x)$ to include a source term $n_{\omega_1}E_{\omega_1}$ at the second-harmonic frequency $2\omega_1$, another $n_{\omega_2}E_{\omega_2}$ at $2\omega_2$, and two terms $n_{\omega_1}E_{\omega_2}+n_{\omega_2}E_{\omega_1}$ at the sum and difference frequencies $\omega_1\pm\omega_2$. Since the interaction term at 30 MHz has two source terms, its amplitude should be about 6 dB greater than those of the second-harmonic terms at 28 and 32 MHz; this was experimentally confirmed. In addition, the interaction strain term $S_{\omega_1+\omega_2}$ should be proportional to $S_{\omega_1}S_{\omega_2}$ or $(S_{2\omega_1}S_{2\omega_2})^{1/2}$; therefore a log-log plot of $S_{2\omega_1}S_{2\omega_2}$ vs $S_{\omega_1+\omega_2}$ should yield a straight line with a slope of 2. This experimental result is shown in Fig. 1. Further, the relation of the 28-, 30-, and 32-MHz output-signal amplitudes to the fundamental amplitudes was observed to follow closely the predicted square-law dependence.

Table I. Output signals produced by the four-wave interaction of three collinear input signals at 9, 9.5, and 22.5 MHz.

Input (MHz)	Output (MHz)	Number of source terms	Relative amplitude observed
9+9.5+11.5	30	6	2.3
9+9+9.5	27.5	3	0.2
9+9.5+9.5	28	3	0.5
9+9+11.5	29.5	3	1.25
9.5+9.5+11.5	30.5	3	0.4
9+11.5+11.5	32	3	0.4
9.5+11.5+11.5	32.5	3	0.1
9+9+9	27	1	<0.05
9.5+9.5+9.5	28.5	1	<0.05
11.5+11.5+11.5	34.5	1	<0.05

A similar experiment, using the same ultrasonic amplifier, has been performed with three collinear, input acoustic waves at frequencies of 9, 9.5, and 11.5 MHz to observe a four-wave interaction. For three input signals many four-phonon processes are possible, and as indicated in Table I, all of the sum frequencies were experimentally observed. Difference frequencies such as $2\omega_1-\omega_2$, etc., have also been observed.

By analogy with the three-wave-interaction problem, the number of source terms contributing to each of the output signals may be readily computed. In particular, since the 30-MHz signal is generated by six source terms, its amplitude is expected to be much larger than those of the third harmonics, and in fact, these signals at 27, 28.5, and 34.5 MHz were difficult to observe, being more than 30 dB smaller than the 30-MHz interaction term. Their small size can be further explained by noting that both the conductivity and drift voltage were optimized for the production of the maximum 30-MHz signal. Additional experimentation utilizing the output signals and at 29.5 and 30 MHz confirmed their dependence on the cube of the input signal amplitudes. This result is shown in Fig. 2.

To establish the electron-phonon interaction as the source of the observed nonlinear mixing, the drift field was removed, two signals at 14 and 16 MHz applied to the input transducer, and the crystal illumination initially adjusted to produce the maximum 30-MHz sum-frequency output. This occurred in the same region as the maximum attenuation of the funda-

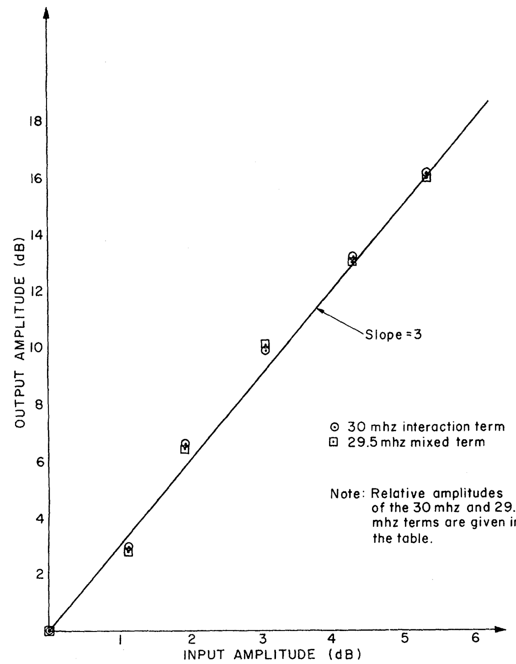

FIG. 2. Four-phonon process, outputs $S_{\omega_1+\omega_2+\omega_3}$ and $S_{2\omega_1+\omega_3}$ versus input amplitude $S_{\omega_1}+S_{\omega_2}+S_{\omega_3}$.

mentals. Then, by placing the illumination at its maximum, the sum-frequency amplitude was reduced by more than 18 dB while the fundamental amplitudes increased by about 10 dB. Similar results were obtained in the four-phonon case. Had this mixing been due to the transducers or the associated electronic equipment, then an increase in the fundamental amplitudes would have produced a corresponding increase in the amplitude of the sum-frequency term. As this relationship did not exist, and further, since the response of the 14-, 16-, and 30-MHz signals to changes in illumination correlates well with previous nonlinear electron-phonon interaction theories,[1,2] the observed mixing of the acoustic waves must have taken place within the cadmium sulfide.

In conclusion, by utilizing the ultrasonic amplifier under gain conditions, large-amplitude three- and four-phonon processes have been observed. The results obtained qualitatively confirm the nonlinear theory of multiple-wave interactions.

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ELASTIC MODULI AND DEBYE TEMPERATURES OF THE POLYCRYSTALLINE RARE-EARTH METALS AT 4.2 AND 300°K

M. Rosen
Atomic Energy Commission, Nuclear Research Center, Negev, Beer-Sheva, Israel
(Received 9 August 1967)

The low-temperature behavior of the rare-earth metals has been subjected to extensive studies from both theoretical and experimental points of view. However, interpretation of several experiments, for instance specific heat, magnetostriction, behavior under high pressure, etc., could be accomplished to a limited extent only because of the unavailability of data on the elastic moduli and Debye temperatures in the vicinity of the absolute zero. The lack of the low-temperature elasticity data on the rare-earth metals is mostly due to the difficulties in performing successful ultrasonic measurements in substances that undergo phase changes. In such cases, the choice of suitable ultrasonic couplants can be a difficult problem.

In the present Letter, we report the polycrystalline values of the Young's and shear moduli, the adiabatic compressibility, Poisson's ratio, and the Debye temperatures at 4.2 and 300°K. They are listed in Table I. These are preliminary results of a comprehensive study on the variation of the elastic moduli and ultra-