

Electronic Effect in the Third-Order Elastic Constant C_{456} of n -Germanium

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The doping of germanium with $\sim 3 \times 10^{19}/\text{cm}^3$ arsenic atoms has been observed to change the magnitude and reverse the sign of the third-order elastic constant C_{456} . Room-temperature measurements of the change of C_{456} and of the change of the shear modulus C_{44} upon doping are reported for two degenerate samples relative to a pure sample. By attributing these impurity effects to the electronic mechanism proposed by Keyes, the shear deformation potential constant Ξ_u is found to be 17.0 ± 0.2 eV, and the carrier densities of the degenerate samples are determined, in excellent agreement with the results of transport measurements.

INTRODUCTION AND EXPERIMENT

THE strain produced by uniaxial stress or associated with an acoustic wave may induce transfer of electrons among conduction band minima, or "valleys," in a many-valleyed semiconductor through the deformation potential effect.¹ Keyes showed² that such transfer produces a reduction of the electronic contribution to the crystal free energy, and a consequent change in the elastic constants, which are the strain derivatives of the free energy. Reduction of the shear modulus C_{44} in germanium upon heavy n -type doping was observed by Bruner and Keyes³ and confirmed the existence of the electronic effects. In the present work, the additional knowledge of the change in the third-order elastic constant C_{456} upon doping permits the determination of crystal electronic properties from fundamental thermodynamic principles.

C_{456} and C_{44} were determined for three samples, one pure and two heavily doped, at room temperature. The velocities of [100] shear waves at 12 Mc were measured to within 0.005% using a phase comparison technique. From these and the sample densities of (5.322 ± 0.002) g/cm³, the values of C_{44} listed in Table I were obtained.

TABLE I. The shear elastic constant C_{44} and the third-order elastic constant C_{456} of germanium at 298°K; units of 10^{12} dyn/cm².

Specimen	C_{44}	C_{456}
Pure (I)	0.6679	-0.500
Heavily doped (II)	0.6427	+1.067
Heavily doped (III)	0.6409	+0.995

C_{456} was determined from the changes in the transit time of ultrasound produced by a uniaxial [011] stress, for polarization of the [100] shear waves parallel and perpendicular to the stress. Blume's ultrasonic interferometer⁴ measured the transit time changes with a resolution of one part in 10^7 as a continuous function of the stress. Values of C_{456} obtained from the data, using the convenient formalism of Thurston and Brugger,⁵ are presented in Table I in their notation. The magnitude of the doping effect is remarkable.

¹ See, for example, C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

² R. W. Keyes, IBM J. Res. Develop. **5**, 266 (1961).

³ L. J. Bruner and R. W. Keyes, Phys. Rev. Letters **7**, 55 (1961).

⁴ R. J. Blume, Rev. Sci. Instr. **34**, 1400 (1963).

⁵ R. N. Thurston and K. Brugger, Phys. Rev. **133**, A1604 (1964); K. Brugger, *ibid.* **133**, A1611 (1964).

INTERPRETATION AND DISCUSSION

Keyes² has derived the following expressions for the electronic contribution at temperature T to C_{44} :

$$\delta C_{44} = -NkT(\Xi_u/3kT)^2[F_{1/2}'/F_{1/2}(\eta_0)] \quad (1)$$

and to C_{456} :

$$\delta C_{456} = -NkT(\Xi_u/3kT)^2[F_{1/2}''/F_{1/2}(\eta_0)]. \quad (2)$$

Here, Ξ_u is the shear deformation potential constant,¹ $F_{1/2}(\eta_0)$ is the Fermi integral as usually defined, η the Fermi energy divided by kT , η_0 is η for the unstrained crystal, and the primes indicate first and second derivatives of $F_{1/2}$ with respect to η , evaluated at η_0 . To determine N and Ξ_u , an additional relation is necessary to fix η_0 :

$$N = 16\pi(2m^*kT/h^2)^{3/2}F_{1/2}(\eta_0), \quad (3)$$

where m^* is the density-of-states effective mass for a single valley. The total carrier density is unaffected by strain in degenerate material.

From the data of Table I, taking $m^* = 0.22m_0$, Eqs. (1)–(3) yield the values of Ξ_u and N presented in Table II. The right-hand column of Table II gives the carrier concentration of the two degenerate samples determined from conductivity and Hall effect measurements.⁶ Sample II was found to be somewhat less homogeneous than sample III, but in both cases the agreement between the two methods of determining the carrier concentration is excellent. The values found for the shear deformation potential element Ξ_u at room temperature agree well with those obtained around liquid nitrogen temperature from various experiments, 16–17 eV,⁷ although somewhat lower than the value

TABLE II. Values of the shear deformation potential Ξ_u , in eV, and carrier concentration N , in units of $10^{19}/\text{cm}^3$, from the data of Table I. The last column lists the carrier concentration N' determined from transport measurements.^a

Specimen	Ξ_u	N	N'
Highly doped (II)	16.9 ± 0.2	2.4 ± 0.1	2.4 ± 0.3
Highly doped (III)	17.1 ± 0.2	2.8 ± 0.1	2.8 ± 0.1

^a See Ref. 6.

⁶ I am indebted to S. R. Baliozian for making these measurements. In the determination of the carrier concentration, a mobility anisotropy, μ_1/μ_{11} , of four was assumed.

⁷ G. Weinreich, T. M. Sanders, Jr., and H. G. White, Phys. Rev. **114**, 33 (1959); C. Herring, T. H. Geballe and J. E. Kunzler, Bell System Tech. J. **38**, 657 (1959) with Ref. 1; J. J. Hall (unpublished).

obtained at helium temperature, 19.2 eV.⁸ It is thus concluded that Keyes' theory of the electronic contribution to the elastic constants for degenerate material accounts quantitatively for the effects here observed.

In the interpretation of this experiment, it has been assumed that the density of states in the neighborhood of the Fermi level is parabolic, so that in Eq. (3) one may insert a constant effective mass. Keyes has shown² that a study of the temperature dependence of δC_{44} and/or δC_{456} can provide m^* directly. Such a study for different doping levels might then permit direct deter-

⁸ H. Fritzsche, Phys. Rev. **115**, 336 (1959).

mination of the energy dispersion of the conduction band to substantial energies above the band edge point. A study of the temperature dependence of the elastic constants of samples I and III is now in progress.

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Multiple-Pulse Nuclear Magnetic Resonance Transients in Solids*

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The response of a spin system is calculated when a pair of 90° rf pulses is applied to a set of static identical interacting nuclei, initially polarized in an external static magnetic field. For pulse spacings the order of the spin-spin relaxation time, a "solid echo" is predicted. This effect is strongly dependent on the relative phasing of the two pulses and is maximized for a 90° phase shift. Extending the work of Powles and Strange, it is shown that the second moment of the nuclear resonance absorption line can be obtained from the solid echo in a straightforward manner, and to a predictable accuracy. A general expression is derived for the principal error term arising in the estimation of the second moment by the solid-echo technique and is applicable to a system of static interacting nuclei of any spin I . Preliminary experimental data shows the presence of solid echoes in powdered aluminum ($I = \frac{3}{2}$). An experimental estimate of the second moment gives $\Delta M_2 = 9.5 \pm 0.2 \text{ G}^2$ at 297°K. The effect of two closely spaced rf 90° pulses has also been calculated for a system of static interacting spins composed of two magnetic species. The rf pulses are assumed to interact with one species only. Some new and interesting effects are predicted, especially in the case when the two pulses are coherent. Unlike a single-spin species where this pulse combination would give zero signal, the presence of the second magnetic ingredient gives rise to a signal the initial slope of which is proportional to the second-moment contribution of the nonresonant spins. Direct measurement of this "cross second moment" should be very valuable, particularly when scalar interactions are present as well as the dipolar interaction. The automatic removal of the resonant spin contribution to the total second moment would tend to increase the accuracy of a scalar coupling constant determination, particularly if the resonant spin term were dominant. Preliminary experiments on a single crystal of NaF show general qualitative agreement with the predictions. Also calculated is the double-pulse response of a single magnetic species with half-integral spin which has both a dipolar and quadrupolar interaction. The system treated is one of well resolved quadrupole satellites. The rf is assumed to interact with the central transition only. Kambe and Ollom have calculated the second moment of the steady-state absorption line of the central transition due to dipolar broadening in the case of well-resolved quadrupole structure. In the present work, it is shown that, as might be expected, the second moment as derived from the free induction decay, when the central line only is pulsed, is in agreement with that of Kambe and Ollom. If a second pulse is applied to the system, in phase with the first, a nonzero signal is predicted, even though this is a single-spin species. It is shown that the growth of this signal is characterized by only part of the dipolar interaction, and a second moment which can be extracted is analogous to the "cross second moment" of a two-spin-species system. When a scalar interaction is present as well as the dipolar term, the nontrivial fact is shown that for two pulses the interaction measured is no longer a simple fraction of the steady-state second moment. The scalar coupling constants and the dipolar lattice sums are shown to be combined in a different way in each case, so that a double-pulse experiment will yield new information on the spin system. This should certainly help in estimating the scalar coupling constants further than just nearest neighbors.

I. INTRODUCTION

IT has been shown previously¹ that if two short 90° rf pulses are applied within a time of order T_2 and

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at the Larmor frequency, to a variety of polarized protonous solids, the system gives rise to a "solid echo" following the second pulse. The echo maximum can rise almost to the full free induction decay amplitude

¹ P. Mansfield, Ph.D. thesis, London University, 1962 (unpublished).