[5] S. Bloom and T. K. Bergstresser, Phys. Status Solidi **42**, 191 (1970).

[6] C. R. Whitsett, S. L. Lehoczky, and J. G. Broerman, Bull. Am. Phys. Soc. **15**, 315 (1970).

[7] L. Liu and D. Brust, Phys. Rev. Lett. **20**, 651 (1968).

[8] D. Sherrington and W. Kohn, Phys. Rev. Lett. **21**, 153 (1968).

[9] J. G. Broerman, Phys. Rev. Lett. **25**, 1658 (1970); Phys. Rev. B **5**, 397 (1972).

[10] J. G. Broerman, Phys. Rev. B **1**, 4658 (1970); Phys. Rev. B **2**, 1818 (1970).

[11] J. G. Broerman, J. Phys. Chem. Solids **32**, 1263 (1971).

[12] D. Sherrington, J. Phys. C **4**, 2771 (1972).

[13] S. A. Aliev, L. L. Korenblit, and S. S. Shalyt, Fiz. Tverd. Tela **8**, 705 (1966) [Sov. Phys.-Solid State **8**, 565 (1966)].

[14] A. V. Ioffe and A. F. Ioffe, Fiz. Tverd. Tela **2**, 781 (1960) [Sov. Phys.-Solid State **2**, 719 (1960)].

[15] M. Rodot, H. Rodot, and R. Triboulet, J. Appl. Phys. **32**, 2254 (1961).

[16] C. R. Whitsett, J. Appl. Phys. **32**, 2257 (1961).

[17] T. C. Harman, J. Phys. Chem. Solids **25**, 931 (1964).

[18] F. Kelemen, E. Cruceanu, and D. Niculescu, Phys. Status Solidi **11**, 865 (1965).

[19] I. A. Smirnov and S. A. Aliev, Fiz. Tverd. Tela **10**, 2643 (1968) [Sov. Phys.-Solid State **10**, 2080 (1969)].

[20] C. R. Whitsett and D. A. Nelson, J. Cryst. Growth **6**, 26 (1969).

[21] C..R. Whitsett and D. A. Nelson, Phys. Rev. B **5**, 3125 (1972).

[22] J. Callaway, Phys. Rev. **113**, 1046 (1959).

[23] G. A. Slack and S. Galginaitis, Phys. Rev. **133**, A253 (1964).

[24] P. G. Klemens, Proc. Phys. Soc. Lond. A **68**, 1113 (1955).

[25] H. E. Swanson, N. T. Gilfrich, and M. I. Cook, Circ. U.S. Natl. Bur. Std. 7, 35 (1957).

[26] H. B. G. Casimir, Physica (Utr.) **5**, 47 (1938); Physica (Utr.) **5**, 320 (1938); Physica (Utr.) **5**, 619 (1938).

[27] R. Berman, F. E. Simon, and J. M. Ziman, Proc. R. Soc. A **220**, 171 (1953).

[28] R. Berman, E. L. Foster, and J. M. Ziman, Proc. R. Soc. A **231**, 130 (1955).

[29] See, for example, J. M. Ziman, *Electrons and Phonons* (Oxford U. P., London, 1963), p. 330.

[30] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).

[31] C. R. Whitsett, Phys. Rev. **138**, A829 (1965).

[32] M. Wagner, Phys. Rev. **131**, 1443 (1963).

[33] J. A. Krumhansl, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon, Oxford, England, 1964), p. 523.

[34] M. G. Holland, Phys. Rev. **132**, 2461 (1963).

[35] In a preliminary report [D. A. Nelson, J. G. Broerman, E. C. Paxhia, and C. R. Whitsett, Phys. Rev. Lett. **22**, 884 (1969)], a similar analysis was presented for HgSe 3-2, 3-3, 3-4, and 3-5 (denoted, respectively, as runs 1–4). In this earlier paper, the data had not been corrected for radiation-loss errors, the electronic thermal conductivity was underestimated, and boundary scattering alone was assumed to dominate at low temperatures. The combination of these factors was responsible for the scattering parameter values then reported being different from the values given here.

[36] A. Lehoczky, D. A. Nelson, and C. R. Whitsett, Phys. Rev. **188**, 1069 (1969).

[37] D. W. Marquardt, J. Soc. Ind. Appl. Math. 11, 431 (1963).

[38] The probability for the confidence limits was based upon Snedecor's $\mathfrak{F}$ (variance ratio) distribution tables in *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun, Natl. Bur. Std. (U. S.) Appl. Math. Ser. 55 (U. S. GPO, Washington, D. C., 1964), pp. 986-9.

[39] W. Zawadski and W. Szymanska, Phys. Status Solidi **45**, 415 (1971).

[40] P. G. Klemens, Solid State Phys. **7**, 1 (1958).

[41] G. Leibfried, in *Handbuck der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, Pt. I, p. 104.

[42] M. Blackman, Philos. Mag. **19**, 989 (1935).

[43] S. Takeno, Prog. Theor. Phys. **29**, 191 (1963).

[44] G. B. Wright, A. J. Strauss, and T. C. Harman, Phys. Rev. **125**, 1534 (1962).

[45] R. R. Galazka, W. M. Becker, and D. G. Seiler, in *Physics of Semimetals and Narrow-Gap Semiconductors*, edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 481.

[46] M. Grynberg, R. Le Toullec, and M. Balkanski, Phys. Rev. B (to be published).

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Ultrasonic Attenuation in Pure and Doped *n*-Type Germanium

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Attenuation suffered by compressional and shear acoustic waves propagating along the ⟨100⟩ and ⟨110⟩ directions has been evaluated from measured third-order elastic moduli for germanium metal in its pure and doped states at room temperature. The present results for pure germanium are in excellent agreement with previous attenuation measurements. As an effect of doping, an increase in phonon viscosity and in thermoelastic attenuation is observed. The resisting force acting against moving dislocations of both types is also presented.

I. INTRODUCTION

The transfer of acoustic energy into thermal-phonon energy accounts for a major part of the acoustic-wave attenuation in crystals. Of the three principal thermal causes[1] of ultrasonic attenuation in solids, only the phonon-viscosity mechanism and the thermoelastic phenomenon provides some non-negligible contributions for dielectric crystals.[2] In the former process, energy conversion takes place at different temperatures owing to thermal conduction between phonons, while in the latter it occurs because of the thermal conduction between compressed and rarefied parts of the propagating wave. The electron-viscosity attenuation would be negligible because of the lack of free electrons in germanium. The present interest is in studying the variation in acoustic-wave propagation parameters caused by doping such a nonconductor with an impurity. Drabble and Fendley[3] have recently published some third-order–elastic-moduli (TOEM) data (measured using a singaround technique) for pure and doped germanium. Their results for pure and n-type doped germanium with a doping concentration of 2.5×10^{18} atoms/cm^3 are given in Table I. Using these and other appropriate data,[4] attenuation of compressional waves propagating along the ⟨100⟩ and ⟨110⟩ directions has been evaluated at 298 °K. For both the screw and edge dislocations, viscous drag, which represents the extent of their interaction with phonons, has been obtained by considering shear and compressional phonon viscosities.

II. THEORY

The thermal relaxation time for the exchange of acoustic-phonon energy into thermal-phonon energy is

$$\tau_{\mathrm{th}}=\frac{3K}{C_v\langle V\rangle^2}\ , \tag{1}$$

where K is thermal conductivity. For longitudinal waves the value becomes twice the above. The Debye average velocity $\langle V\rangle$ is given by

$$\langle V\rangle=\frac{1}{\sqrt{\rho}}\left(\frac{c_{11}^{-3/2}+2c_{44}^{-3/2}}{3}\right)\quad . \tag{2}$$

When the time period of the propagating wave is much greater than the thermal-phonon relaxation time, the attenuations due to the phonon-viscosity mechanism α_P and to the thermoelastic phenomenon α_T are[5]

$$\alpha_P=\frac{\Omega^2E_0D_l\tau_l}{6\rho V_l^3}\ ,\qquad \alpha_T=\frac{\Omega^2\langle\gamma\rangle^2KT}{2\rho V_l^5}\ , \tag{3}$$

where Ω is the angular frequency of the acoustic wave. Similar equations with D_l, τ_l, and V_l replaced by D_s, τ_s, and V_s, respectively, hold for shear waves. Here $\tau_l=2\tau_{\mathrm{th}}$, E_0 is the thermal-energy density, and D, the nonlinearity constant, is expressed as

$$D=9\langle\gamma^2\rangle-\frac{3C_vT\rho}{E_0}\ \langle\gamma\rangle^2\ , \tag{4}$$

where $\langle\gamma\rangle$ and $\langle\gamma^2\rangle$ are the Grüneisen number and its square averaged over 39 pure modes for each direction of propagation. The mathematical formulation for the dislocation drag constant is the same as discussed earlier.[6]

TABLE I. Third-order elastic moduli for pure and doped n-type germanium (in units of 10^{12} dyn/cm^2).

	Pure Ge	Doped Ge
c_{111}	−6.81	−7.72
c_{112}	−3.63	−4.27
c_{123}	−0.09	−0.83
c_{144}	0.09	−0.05
c_{166}	−3.06	−3.10
c_{456}	−0.43	0.35

TABLE II. Grüneisen number and acoustic coupling constant for pure and doped n-type germanium at 298 °K.

		Pure Ge			Doped Ge		
Direction	Mode	$\langle\gamma\rangle$	$\langle\gamma^2\rangle$	$(\frac{1}{3}D)$	$\langle\gamma\rangle$	$\langle\gamma^2\rangle$	$(\frac{1}{3}D)$
⟨100⟩	Compressional	0.703	1.007	2.274	0.823	1.305	2.890
	Shear	0.000	0.129	0.387	0.000	0.222	0.665
⟨110⟩[a]	Compressional	0.813	0.861	1.585	0.856	1.074	2.114
	Shear	0.000	0.939	2.817	0.000	0.838	2.514

[a] For shear waves the polarization is along $\langle 1\bar{1}0\rangle$.

III. RESULTS AND DISCUSSION

From the available second-order–elastic-moduli (SOEM) data[7] and other thermodynamic data, some of the results obtained for pure Ge are listed as follows:

$V_l=4923$ m sec^{-1} , $V_s=3550$ m sec^{-1} ,

$K=16.45\times10^{-2}$ cal cm^{-1} sec^{-1} °K^{-1} ,

$C_v=0.311\times10^7$ erg g^{-1} °K^{-1} ,

$E_0=3.252\times10^9$ erg cm^{-3} ,

$\tau_{\mathrm{th}}=8.487\times10^{-12}$ sec.

For a doping concentration of 2.5×10^{18} atoms/cm^3 the change in density and thermal-conductivity values is less than 0.1%. Except C_{456}, other TOEM do not exhibit any significant change as an effect of change in electronic concentration, and so SOEM will be still less affected. Hence the above parameters would be more or less the same for doped germanium.

Table II lists $\langle\gamma\rangle$, $\langle\gamma^2\rangle$, and the acoustic coupling constant D at 298 °K. Since the doping does not change the cubic nature of germanium lattice, Mason's theoretical formulas[8,9] are still applicable. The elements lying on second and fourth rows crossing third and sixth columns are zero, which means that there is no change in volume and hence no thermoelastic attenuation for shear waves. For compressional waves propagating along the ⟨100⟩ direction, the present values of $\langle\gamma\rangle=0.703$ and $D=6.82$ lie between the results of Bateman *et al.*[10]

TABLE III. Acoustic-wave propagation parameters for pure and doped germanium at 298 °K.

Direction	Metal	$(\alpha/f^2)_P$[a] Compressional	$(\alpha/f^2)_P$[a] Shear	$(\alpha/f^2)_T$[a] Compressional	B_{screw}(mP) Compressional	B_{screw}(mP) Shear	B_{edge}(mP) Compressional	B_{edge}(mP) Shear
⟨100⟩	Pure Ge	34.03	7.72	1.14	9.91	0.76	15.09	1.73
	Doped Ge	43.25	13.26	1.56	11.33	1.30	20.32	2.77
⟨110⟩[b]	Pure Ge	23.72	57.49	1.52	6.21	5.52		
	Doped Ge	31.63	50.14	1.69	8.29	4.93		

[a] The unit of (α/f^2) is 10^{-18} dB sec^2 cm^{-1}.

[b] For shear waves the polarization is along the $\langle 1\bar{1}0\rangle$ direction.

($\langle\gamma\rangle = 0.725$ and $D = 7.0$) and Drabble and Gluyas[11] ($\langle\gamma\rangle = 0.615$ and $D = 5.45$). As a result of doping there is a general increase in all these parameters.

Considering the contributions from the two thermal phenomena, the total ultrasonic attenuation for compressional and shear waves propagating along the ⟨100⟩ direction is shown in Fig. 1. The solid line is for pure germanium while the dash-dotted line corresponds to doped Ge. These contributions have been separately presented in Table III. The experimental points of Lamb *et al.*,[12] Dobbs *et al.*,[13] and Bateman[14] for compressional waves and those of Redwood[15] and Bateman[14] for shear waves almost lie on the corresponding theoretical curves.

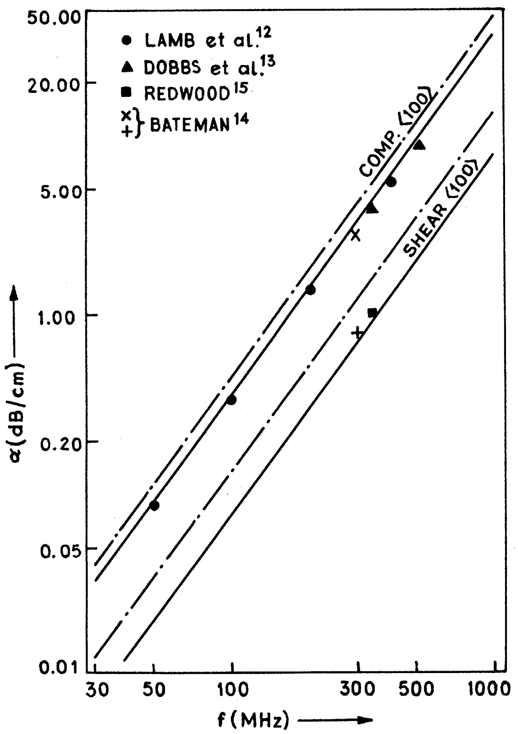

FIG. 1. Square-law attenuation of ultrasonic waves propagating along the ⟨100⟩ direction in pure and doped germanium at 298 °K (dashed line, pure Ge; dash-dotted line, doped Ge). Different points correspond to various experimental results for pure germanium.

It is observed that, because of doping, the total ultrasonic attenuation for longitudinal and transverse waves increases by about 27 and 73%, respectively. The results obtained here for doped germanium have no experimental counterparts (to the authors' knowledge), and all the points marked are for pure germanium. A similar set of curves may be drawn for propagation along the ⟨110⟩ direction. But there the attenuation of shear waves decreases on doping, which may be attributed to the abnormal increase in C_{456} at room and liquid-nitrogen temperatures. Keyes's[16] explanation of change in doping contribution to the free energy and hence the energy levels in the conduction band as a function of strain appears to be sufficient, because then a slight decrease in thermal conductivity will account for this smaller attenuation.

Doping, which tends to convert an insulator into a semiconductor, is accompanied by an increase in the acoustic coupling constant D and hence in the phonon viscosity. This increased viscosity creates a greater resistance against the motion of moving dislocations; this is shown as an increment in the value of drag constants in Table III. The direct contribution of electron viscosity remains negligible always.

IV. CONCLUSIONS

As a result of doping, a general increase ranging from 25 to 86% in different propagation parameters is observed. For the ⟨100⟩ direction, the thermoelastic attenuation (being directly governed by thermal conductivity) is affected to a greater extent than the Akhieser attenuation, and shear-wave parameters (α_P, B_{screw}, and B_{edge}) show a greater response than their compressional counterparts. A deeper study of the doping effect over a vast temperature may reveal a further demonstration of the electronic contribution to the propagation parameters when an insulator is converted into a semiconductor.

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[1] W. P. Mason and A. Rosenberg, J. Acoust. Soc. Am. **45**, 470 (1969).

[2] S. K. Kor, U. S. Tandon, and Gulshan Rai, Phys. Rev. B **5**, 4143 (1972).

[3] J. R. Drabble and J. Fendley, Solid State Commun. **3**, 269 (1965).

[4] *American Institute of Physics Handbook* (McGraw–Hill, New York, 1963).

[5] *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1965), Vol. III B, Chap. VI.

[6] S. K. Kor, U. S. Tandon, and G. Rai, Phys. Rev. B **6**, 2195 (1972).

[7] H. J. McSkimin and P. Andreatch, Jr., J. Acoust. Soc. Am. **36**, 3312 (1964).

[8] W. P. Mason and T. B. Bateman, J. Acoust. Soc. Am. **36**, 645 (1964).

[9] W. P. Mason, J. Acoust. Soc. Am. **42**, 253 (1967).

[10] T. B. Bateman, W. P. Mason, and H. J. McSkimin, J. Appl. Phys. **32**, 928 (1961).

[11] J. R. Drabble and M. Gluyas, in Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963 (unpublished).

[12] J. Lamb, M. Redwood, and Z. Steinschlifer, Phys. Rev. Lett. **3**, 28 (1959).

[13] E. R. Dobbs, B. B. Chick, and R. Truell, Phys. Rev. Lett. **3**, 332 (1959).

[14] W. P. Mason, in *Physical Acoustics*, edited by A. W. P. Mason (Academic, New York, 1965), Vol. III B, p. 249.

[15] M. Redwood, Proc. Phys. Soc. Lond. B **70**, 721 (1957).

[16] R. W. Keyes, IBM J. Res. Dev. **5**, 266 (1961).

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Phonon Contribution to the Free Energy of Interacting Adatom Pairs

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The free energy ΔF due to the interaction through the crystal phonon field of two identical atoms adsorbed on a (100) surface of a simple cubic monatomic lattice is studied within the framework of the Montroll–Potts model. The zero-point energy of interaction, ΔE_0, is found analytically in the limit of large separation distances, and numerical results are presented for small separation distances. The leading temperature-dependent terms in the expansion of ΔF are given in closed form in both the low- and high-temperature limits. The results are given as a function of the mass and separation distance of the adsorbed atoms and as a function of the force constant binding the adsorbed atoms to the surface. For all values of the model parameters, it is found that the free energy decreases with the separation distance. Thus, two adatoms on a surface are attracted toward each other.

I. INTRODUCTION

Recently, chemisorption, and to a lesser degree physisorption, has been extensively studied in several laboratories. The well-defined patterns within the surface adlayer are often different in structure from the surface layer of the absorbate.[1] Of fundamental importance in understanding these various patterns is an understanding of the interaction energy between pairs of adatoms.

Recently, Einstein and Schrieffer[2] have studied the electronic contribution to the energy of interaction at 0 °K (the zero-point energy) of two adatoms on the (001) surface of a simple cubic monoatomic solid within the tight-binding approximation. Their simple non-self-consistent first approach applies mainly to the case of chemisorption of simple gases on transition metals.

In this paper we consider the energy of interaction of two adatoms through the crystal phonon field. It is of interest to know the magnitude of the phonon contribution to the interaction free energy relative to the magnitude of the electronic contribution. Whereas one might expect the phonon contribution to be negligible compared to the electronic contribution, such a conclusion has not been demonstrated.[3] It seems possible, for example, that there might be cases in physisorption of rare-gas atoms on rare-gas crystals where the phonon contribution may be expected to be the major contribution to the free energy of interacting adatom pairs. In addition, Einstein and Schrieffer have found that the interaction energy in the electronic case may vanish depending upon the location of the Fermi level in the band. It should be noted that, like Einstein and Schrieffer, we do not consider direct interactions between the adatoms.

In Sec. II we introduce the phonon model and present the general expressions which enable us to calculate the free energy as a function of temperature. In Sec. III we consider the interaction free energy at 0 °K. For a general separation distance, this zero-point energy ΔE_0 must be calculated numerically. We present results showing how this zero-point energy depends upon separation distance, the mass of the adatoms, and the strength of the force constant binding the adatoms to the surface. In addition, an analytic expression is obtained for ΔE_0 in the limit of weak binding and large separation distances. In Sec. IV, we consider the