9e. Properties of Semiconductors

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9e-1. Introduction. This chapter contains a number of numerical values of semiconductor parameters collected from the literature up to November, 1968. Our knowledge is, however, still very uneven. In some cases very detailed information about band structure, transport properties, etc., is available, while for other semiconductors even the energy gap has not yet been determined unambiguously. The data in this chapter are therefore limited to a few groups: elemental semiconductors, III-V compounds, some II-IV compounds, some II-VI compounds, the lead compounds, and a few others.

For definitions of electronic parameters and some simple formulas the reader is referred to Sec. 9c.

9e-2. Band Structure. In order to illustrate concepts like anisotropic effective mass, spin-orbit splitting, etc., the electronic energy band structure of Ge and Si will be briefly discussed (refs. 1 to 5).

Germanium. CONDUCTION BAND. The constant-energy surfaces near the bottom of the conduction band consist of four symmetrically equivalent ellipsoids, whose lengths are oriented along the ⟨111⟩ directions. The four minima (valleys) are located at the edge of the Brillouin zone. Each of these ellipsoids can be described by the following energy-momentum relation:

$$\varepsilon = \frac{p_x^2 + p_y^2}{2m_t} + \frac{p_z^2}{2m_l}$$

where m_t and m_l are the transverse and longitudinal effective masses, respectively.

The effective mass m^* in any particular direction of momentum space is given by

$$\frac{1}{m^{*2}} = \frac{\cos^2\theta}{m_t^2} + \frac{\sin^2\theta}{m_t m_l}$$

where θ is the angle between the chosen direction and the longitudinal axis of the ellipsoid.

Experiments (ref. 2) indicate that

$$m_l = (1.59 \pm 0.03)m_0$$
$$m_t = (0.082 \pm 0.0003)m_0$$

At the center of the zone (Γ_2'),

$$m^* \approx 0.034m_0$$

The density-of-state effective mass $m^{(N)}$ (or average effective mass), which is obtained from conductivity and Hall-effect experiments, is given by

$$m^{(N)} = (m_l m_t^2)^{\frac{1}{3}} \nu^{\frac{2}{3}}$$

where ν is the number of ellipsoids. The value of this parameter for the conduction band of germanium is $m_e^{(N)} = 0.55m_0$.

VALENCE BAND. The energy-band structure at the top of the valence band consists of three nearly spherical (warped) surfaces. The maxima are located at the center of the zone [$\vec{k} = 0$]. Two of the surfaces are degenerate at the center point. The third is somewhat lower in energy owing to *spin-orbit interaction*. (The spin-orbit interaction results from coupling between the magnetic dipole fields of the spin and the orbital motion of an electron.) Close to the band edge the energies of the two degenerate surfaces V_1 and V_2 can be described by

$$\mathcal{E}_{1,2} = -\frac{1}{2m_0}\{Ap^2 \pm [B^2p^4 + C^2(p_x^2p_y^2 + p_y^2p_z^2 + p_z^2p_x^2)]^{\frac{1}{2}}\}$$

and that of the split-off band V_3 by

$$\mathcal{E}_3 = -\Delta - \frac{1}{2m_0}Ap^2$$

where Δ is the spin-orbit splitting energy. The plus sign in the expression for $\mathcal{E}_{1,2}$ refers to light holes, and the minus sign to heavy holes. In Ge the parameters have the following values:

$\Delta = 0.29$ ev	$m_{V_1} = 0.34m_0$
$A = -13.3 \pm 0.2$	$m_{V_2} = 0.043m_0$
$B = \pm 8.6 \pm 0.1$	$m_{V_3} = 0.08m_0$
$C = \pm 12.5 \pm 0.2$	

For further details see Fig. 9e-1.

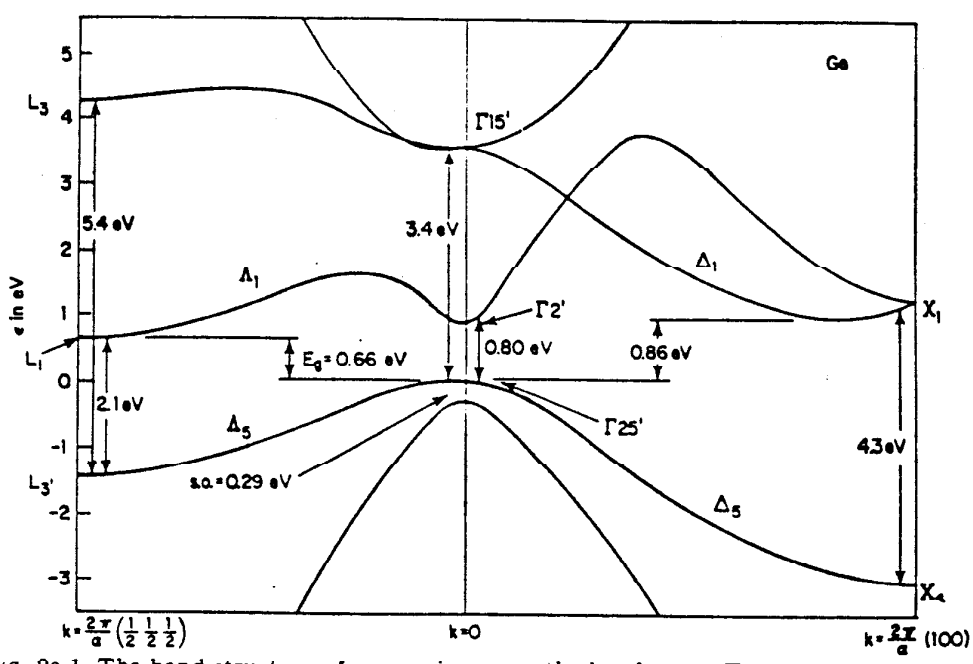

FIG. 9e-1. The band structure of germanium near the band gap. Energy as a function of wave vector k for the ⟨111⟩ and ⟨100⟩ directions. (*After Charles Kittel, "Introduction to Solid State Physics," 3rd ed., John Wiley & Sons, Inc., New York,* 1966.)

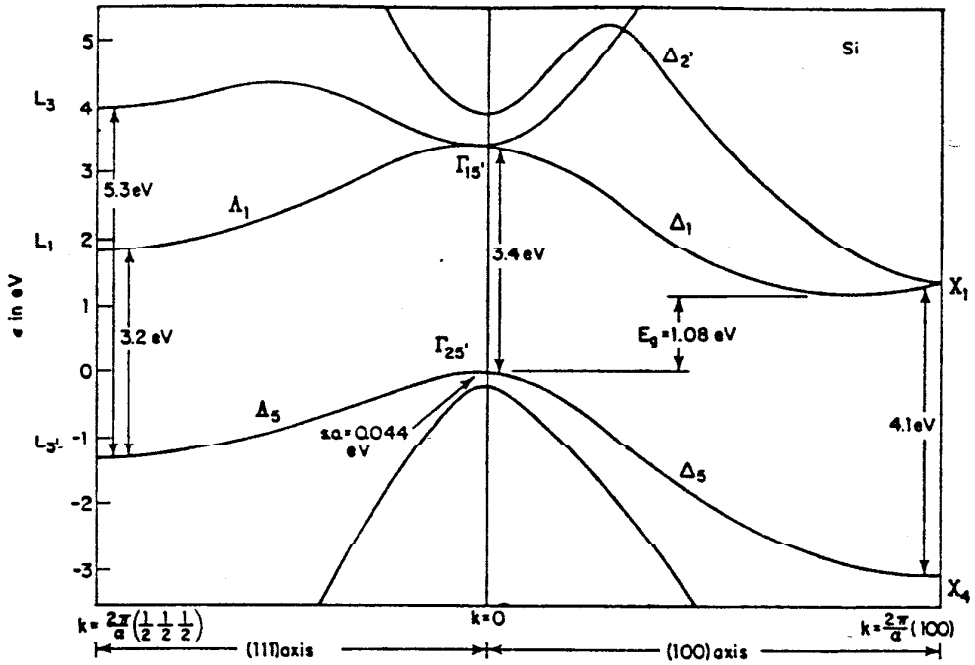

FIG. 9e-2. The band structure of silicon near the band gap. Energy as a function of wave vector k for the ⟨111⟩ and ⟨100⟩ directions. (*After Charles Kittel, "Introduction to Solid State Physics," 3d ed., John Wiley & Sons, Inc., New York*, 1966.)

Silicon. CONDUCTION BAND. The constant-energy surfaces near the bottom of the conduction band consist of three symmetrically equivalent ellipsoids whose length axes are oriented along ⟨100⟩ directions. The six minima (valleys) are inside the Brillouin zone.

The effective electron mass values are

$$m_l = (0.98 \pm 0.04)m_0$$
$$m_t = (0.19 \pm 0.01)m_0$$

The density-of-states effective mass is

$$m_e^{(N)} = 1.1m_0$$

VALENCE BAND. The constant-energy surfaces are similar to those of germanium at the top of the valence band. The parameters for Si are

$$\Delta = 0.044 \text{ eV} \qquad m_{V_1} = 0.52m_0$$
$$A = -4.0 \pm 0.2 \qquad m_{V_2} = 0.16m_0$$
$$B = \pm 1.1 \pm 0.2 \qquad m_{V_3} = 0.25m_0$$
$$C = \pm 4.1 \pm 0.5$$

For further details see Fig. 9e-2.

References on Band Structure of Ge and Si:

1. Geballe, T. H.: "Semiconductors," p. 313, N. B. Hannay, ed., Reinhold Publishing Corporation, New York, 1959.
2. Kittel, C.: "Introduction to Solid State Physics," 3d ed., p. 316, John Wiley & Sons, Inc., New York, 1966.
3. Cohen, M. L., and T. K. Bergstresser: *Phys. Rev.* **141**, 789 (1966).
4. Aigrain, P., and M. Balkanski, eds.: "Selected Constants of Semiconductors," Pergamon Press, New York, 1961.
5. Putley, E. H.: "The Hall Effect and Related Phenomena," Butterworth & Co. (Publishers), Ltd., London, 1960.

III-V Compounds. The bandstructures of the III-V compounds are similar to those of Ge and Si. However, most of the III-V compounds have the maximum of the valence band and the minimum of the conduction band at the center of the Brillouin zone ($k = 0$). Values of the energy gap E_g, effective masses (electron mass m_e^*, light and heavy hole masses m_{lh}^* and m_{hh}^*, mass of the "split-off" valence band m_{sh}^*, free-electron mass m_0), and spin-orbit splitting $\Delta_{s.o.}$ are listed in the first seven columns of Table 9e-1.

TABLE 9e-1. CHARACTERISTICS OF III-V COMPOUNDS

Compound	ϵ_g at $T = 0$ K, eV		Effective masses				$\Delta_{s.o.}$ eV	Mobilities, cm²/volt-sec at 300 K		Impurity activation energy, eV
	Direct	Indirect	m_e^*/m_0	m_{lh}^*/m_0	m_{hh}^*/m_0	m_{sh}^*/m_0		μ_e	μ_h	
InSb	0.23[6]	.....	0.015	0.021	0.39	0.11(c)	~0.9	78,000	750	0.007 (Zn,p)
InAs	0.36	.....	0.026	0.025	0.41	0.08[3]	0.43	33,000	460	
InP	1.29	.....	0.073	0.078(c)	0.4	0.15(c)	~0.2	4,600	150	
InN	2.4									
GaSb	0.81[4]	.....	0.047	0.06	0.3	0.14(c)	~0.8	4,000	1,400	0.024 (Zn,p)
GaAs	1.52	1.85 (X)†	0.07	0.12	0.68	0.20	0.34	8,800	400	
GaP	2.88 (Γ)†	2.32 (X)†	0.13(c)	0.14(c)	0.86(c)	0.24(c)	0.13	300	100	
GaN	3.3									
AlSb	2.20 (Γ)†	1.65 (X)†	0.11(c)	0.11(c)	0.9	0.22(c)	0.75	200	550	0.07 (Te,n) 0.16 (Se,n)
AlN	4.6									
BP	6.0 (?)	2.0								
Ref.	1, 2		3				4	5		6, 7

† At 77 K.
(c) = calculated.

Other Compounds and Elemental Semiconductors. Somewhat less is known about the band structure of other semiconducting compounds and elements. Values for energy gaps, effective masses, and mobilities can be found in Table 9e-2.

Temperature and Pressure Dependence of the Energy Gap. For most semiconductors the energy gap decreases with increasing temperature. Exceptions are the lead compounds. The change is nearly linear with temperature except at low temperatures. The energy gap also changes with pressure. The thermodynamic relationship between the two is

$$\left(\frac{\partial \mathcal{E}_g}{\partial T}\right)_P = \left(\frac{\partial \mathcal{E}_g}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial \mathcal{E}_g}{\partial P}\right)_T$$

Temperature and pressure coefficients for a few materials are listed in Table 9e-3.

References for Table 9e-1

1. Willardson, R. K., and A. C. Beer, eds.: "Semiconductors and Semimetals," vol. 1, p. 7, Academic Press, Inc., New York, 1966–1968.
2. InN: Ormont, B. F.: *Zh. Neorgan. Khim.* **4**, 2176 (1959); transl.: *Russ. J. Inorg. Chem.* **4**, 988 (1959).
   GaN: Grimmeis, H. G., et al.: *Z. Naturforsch.* **159**, 799 (1960).
   AlN: Ivey, H. F.: *Advan. Electron Electron. Phys.*, suppl. 1, 169 (1963).
   BP: Archer, R. J., et al.: *Phys. Rev. Letters* **12**, 538 (1964).
3. Reference 1, vol. 2, p. 151.
4. Reference 1, vol. 2, p. 141.
5. Reference 1, vol. 1, p. 16.
6. Hannay, N. B., ed.: "Semiconductors," p. 389, Reinhold Publishing Corporation, New York, 1959.
7. AlSb: Turner, W. J., and W. E. Reese: *Phys. Rev.* **117**, 1003 (1960).

TABLE 9e-2. CHARACTERISTICS OF SEVERAL ELEMENTAL AND COMPOUND SEMICONDUCTORS

Compound	Structure	ϵ_g, eV ($T = 0$ K)	Effective masses		Mobilities at 300 K, cm²/volt-sec		References
			m_e/m_0	m_h/m_0	μ_e	μ_h	
Diamond	cub	5.4	0.2	0.7(lh), 2.12(hh) 1.06(sh)	1,800	1,200	1–5
Graphite	hex	0.0	0.03–0.04	0.06–0.07	4×10^5	1.5×10^5 (lh)	6–8
Se	trig	1.8 ($T = 300$ K)	.....	.....	~ 10	.....	8
Te	trig	0.33	$m_e^{long} = 0.37m_0$ $m_e^{trans} = 0.32m_0$	$m_{lh} = 0.08m_0$, $m_{hh} = 0.12m_0$ $m_{sh} = 0.04m_0$	1,700	1,200	8, 9
α-Sn	cub	0.0†	0.02	$m_{lh} = 0.06m_0$, $m_{hh} = 0.3m_0$	2,500	2,400	8, 10a
SiC	hex	3.0	.....	.....	100	50	8
	cub	1.9	.....	.....	.....	.....	8
Mg_2Si	antifluorite	0.78	0.46	.....	400	60	10b
Mg_2Ge	antifluorite	0.57	.....	.....	500	100	8, 11
Mg_2Sn	antifluorite	0.185 (indirect) 0.35 (direct)	.....	.....	320	260	9, 12, 13
Mg_3Sb_2	hex	0.82	0.32‡	0.57‡	19	82	14
Zn_3As_2	tetr	0.93	.....	.....	.....	10	15
$ZnAs_2$	monocl	0.90(‖c), 0.93(⊥c)	.....	.....	.....	50	15
ZnSb	orth	0.56	$m_e^{long} = 0.175m_0$ $m_e^{trans} = 0.146m_0$	.....	340	10	9
Cd_3As_2	tetr	<0.02	0.04	.....	15,000	.....	16
$CdAs_2$	tetr	1.00(‖c), 1.04(⊥c)	$m_e^{long} = 0.15m_0$ $m_e^{trans} = 0.58m_0$	$m_h^{long} = 0.094m_0$ $m_h^{trans} = 0.35m_0$	$\mu^c = 400$ $\mu^a = 100$	.....	15,17
CdSb	orth	0.5–0.6	$m_e^{long} = 0.14m_0$ $m_e^{trans} = 0.16m_0$	.....	250	300–700	8
PbS	f.c.c.	0.29	$m_e^{long} = 0.104m_0$ $m_e^{trans} = 0.08m_0$	$m_h^{long} = 0.105m_0$ $m_h^{trans} = 0.075m_0$	550	600	18a, 18b, 9
PbSe	f.c.c.	0.17	$m_e^{long} = 0.068m_0$ $m_e^{trans} = 0.041m_0$	$m_h^{long} = 0.084m_0$ $m_h^{trans} = 0.0465m_0$	1,020	930	18a, 18c, 9
PbTe	f.c.c.	0.19	$m_e^{long} = 0.23m_0$ $m_e^{trans} = 0.024m_0$	$m_h^{long} = 0.381m_0$ $m_h^{trans} = 0.031m_0$	1,620	750	18a, 18d, 9

ZnO	hex W §	3.436	0.38	1.8	100 [20]	.....	19 (E_g, m^*) 20–22 23, 24 (μ)
ZnS	W §	3.910	$m_\perp = 0.27$, $m_\parallel = 0.28$	$m_\perp = 0.58$, $m_\parallel = ?$	140 [21]	.....	
ZnS	Z §	3.84	.....	.....	.....	.....	
ZnSe	W §	2.795	.....	.....	.....	.....	
ZnSe	Z §	2.83	0.1	0.6	100 [9]	.....	
ZnTe	Z §	2.39	.....	.....	.....	.....	
CdS	W §	2.582	$m_l = 0.171m_0$, $m_t = 0.15m_0$	$m_\perp = 5m_0$, $m_\parallel = 0.7m_0$	210 [8]	.....	
CdSe	W §	1.840	0.13	$m_\perp = 0.45$, $m_\parallel \geq m_0$	600 [22]	.....	
CdTe	Z §	1.607	.....	.....	900 [23]	75 [24]	
HgSe	Z §	−0.24¶	.....	0.17‡	.....	.....	25
HgTe	Z §	−0.30¶	0.027†	0.35‡	.....	.....	
As_2Se_3	amorph.	1.6	.....	.....	.....	.....	
As_2Te_3	monocl.	1.0	.....	.....	170	80	
Sb_2S_3	orthorh.	~1.7	.....	.....	15	45	
Sb_2Se_3	orthorh.	~1.2	.....	.....	.....	270	26
Sb_2Te_3	rhomb.	0.3	.....	.....	.....	.....	
Bi_2S_3	orthorh.	1.3	.....	.....	.....	.....	
Bi_2Se_3	rhomb.	0.35	.....	.....	600	.....	
Bi_2Te_3	rhomb.	0.2	0.45	0.51	1,250	515	26, 27
Cu_2O	cub	2.172	0.5	0.5	.....	100	28*a*, 28*b*, 8
TiO_2	tetr.	‖3.03; ⊥3.04	.....	.....	1.0(‖c); 0.2(⊥c)	.....	9, 29
$SrTiO_3$	cub	3.4	$m_l = 1.5m_0$, $m_t = 6.0m_0$	.....	5	.....	30, 31

† At $k = 0$.
‡ Density-of-states mass.
§ W = wurzite; Z = zincblende.
¶ HgSe and HgTe are semimetals. The "energy gap" quoted is $E(\Gamma_6) - E(\Gamma_8)$ which is negative.

References for Table 9e-2

1. Mitchell, E. J. W.: *J. Phys. Chem. Solids* **8**, 444 (1958).
2. Clark, C. D.: *Proc. Roy. Soc. (London)*, ser. A, **277**, 312 (1964).
3. Rauch, C. J.: *Phys. Rev. Letters* **7**, 83 (1961).
4. Rauch, C. J.: "Proceedings International Conference on the Physics of Semiconductors," p. 276, Exeter, Institute of Physics, London, 1962.
5. Redfield, A. G.: *Phys. Rev.* **94**, 526 (1954).
6. Soule, D. E., and J. W. McClure: *J. Phys. Chem. Solids* **8**, 29 (1959).
7. Soule, D. E.: *Phys. Rev.* **112**, 698 (1958)
8. Putley, E. H.: "The Hall Effect and Related Phenomena," Butterworth & Co. (Publishers), Ltd., London, 1960.
9. Aigrain, P., and M. Balkanski, eds.: "Selected Constants of Semiconductors," Pergamon Press, New York, 1961.

10*a*. Groves, S., and W. Paul: "Proceedings of the International Conference on the Physics of Semiconductors," p. 41, M. Hulin, ed., Dunod, Paris, 1964.

10*b*. Morris, R. G., R. D. Redin, and G. C. Danielson: *Phys. Rev.* **109**, 1909 (1958).

11. Lott, L., and D. Lynch: *Phys. Rev.* **141**, 681 (1966).
12. Lipson, H. G., and A. Kahan: *Phys. Rev.* **133**, 800 (1964).
13. Lawson, W. D., et al.: *J. Electron.* **1**, 203 (1955).
14. Busch, G., et al.: *Helv. Phys. Acta* **27**, 249 (1954).
15. Turner, W. J., et al.: *Phys. Rev.* **121**, 750 (1961).
16. Haidemenakis, E. D., et al.: *J. Phys. Soc. Japan* **21**, 189 (1966).
17. Turner, W. J., et al.: *J. Appl. Phys.* **32**, 2241 (1961).

18*a*. Mitchell, E. D., et al.: "Proceedings International Conference on the Physics of Semiconductors," p. 325, M. Hulin, ed., Dunod, Paris, 1964.

18*b*. Cuff, K. F., et al.: ref. 18*a*, p. 677.

18*c*. Berman, S.: *Phys. Rev.* **158**, 723 (1967).

18*d*. Numata, H., and Y. Uemara: *J. Phys. Soc. Japan* **19**, 2140 (1964).

19. Reynolds, D. C., et al., *Phys. Stat. Solidi* **12**, 3 (1965).
20. Thomas, D. G.: *J. Phys. Chem. Solids* **10**, 47 (1959).
21. Aven, M., and C. A. Mead: *Appl. Phys. Letters* **7**, 8 (1965).
22. Heinz, D. M., and E. Banks: *J. Chem. Phys.* **24**, 391 (1956).
23. Segall, B., et al.: *Phys. Rev.* **129**, 2471 (1963).
24. Yamada, S.: *J. Phys. Soc. Japan* **17**, 645 (1962).
25. Harman, T. C.: "Proceedings of the International Conference on II-V Compounds," p. 982, D. G. Thomas, ed., W. A. Benjamin, Inc., New York, 1967.
26. Black, et al.: *J. Phys. Chem. Solids* **2**, 240 (1957).
27. Drabble, J. R.: *Proc. Phys. Soc. (London)* **71**, 430 (1958); *ibid.*, **72**, 380 (1958).

28*a*. Knox, R. S.: *Solid State Phys.* suppl. 5, 53 (1963).

28*b*. Gross, E. F.: *J. Phys. Chem. Solids* **8**, 172 (1959).

29. Frederikse, H. P. R.: *J. Appl. Phys.* **32** (suppl.), 2211 (1961).
30. Cohen, M. I., and R. F. Blunt: *Phys. Rev.* **168**, 929 (1968).
31. Frederikse, H. P. R., et al.: *J. Phys. Soc. Japan* **21**, (suppl.), 32 (1966).

TABLE 9e-3. TEMPERATURE AND PRESSURE DEPENDENCE OF THE ENERGY GAP

	$(\delta\epsilon g/\delta T)_P$, eV/deg × 10^4	Ref.	$(\delta\epsilon g/\delta P)_T$, eV m²/kg × 10^2	Ref.
C	.....	...	< 1.0 (*X*)	3
Si	− 2.3 (*X*)	1	− 1.5 (*X*)	3
Ge	− 3.7	1	5.0 (*L*)	3
α-Sn	.....	1	5.0 (*L*)	3
Se	−14	2	−20.0	2
Te	− 0.3	2	−19.0	2
SiC	− 3.3	1		
InSb	− 2.9 (Γ)	1	(14.2), 15.5 (Γ)	1
InAs	− 3.3 (Γ)	1	(4.8,5.5)8.5	1
InP	− 4.6 (Γ)	1	4.6, 8.4	
GaSb	− 4.1 (Γ)	1	12.0, (16.0)	1
GaAs	− 5.0 (Γ)	1	−8.7 (*X*) 9.4	1
GaP	− 5.4 (Γ)	1	10.7	1
AlSb	− 3.5 (*X*?)	1	− 1.6 (*X*)	
ZnO (W)	− 9.5 (Γ)	1	0.6 (Γ)	1
ZnS (W)	− 3.8 (Γ)	1	9.0 (Γ)	1
ZnSe (W)	− 7.2 (Γ)	1	6.0 (Γ)	1
CdS (W)	− 5.0 (Γ)	1	+ 3.3 (Γ)	1
CdSe (W)	− 4.6 (Γ)	1	.....	1
PbS	+ 3.7 (*L*)	1	6.9 (*L*)	1
PbSe	~ 4.0 (*L*)	1		
PbTe	~ 4.0 (*L*)	1		

References for Table 9e-3

1. Aigrain, P., and M. Balkanski, eds.: "Selected Constants of Semiconductors," Pergamon Press, New York, 1961.
2. Caldwell, R. S., and H. Y. Fan: *Phys. Rev.* **114**, 664 (1959).
3. Willardson, R. K., and A. C. Beer, eds.: "Semiconductors and Semimetals," vol. 1, p. 200. Academic Press, Inc., New York, 1966–1968.

9e-3. Hall Coefficient and Mobility. The Hall effect is sometimes described by the "Hall angle" θ which is the angle through which the equipotential planes in a long rectangular specimen carrying a current are tilted when a magnetic induction B is applied normal to the direction of current flow. For conduction by electrons or holes only

$$\theta = \mu B$$

For a semiconductor with spherical energy surfaces containing only electrons which are nondegenerate and are scattered by acoustical lattice modes

$$R = \frac{-3\pi}{8}\frac{1}{nec} = \frac{-1.18}{nec}$$

If the scattering is due to ionized impurities, then

$$R = \frac{-315\pi}{512}\frac{1}{nec} = \frac{-1.93}{nec}$$

In case of degeneracy

$$R = -\frac{1}{nec} = \frac{-6.25 \times 10^{18}}{n} \quad \text{cm}^3/\text{coul}$$

For hole conduction n becomes p (= density of holes) and the minus sign changes to a plus sign. The conductivity is given by

$$\sigma = ne\mu$$

where μ is the drift mobility of electrons or holes.

The *Hall mobility* is given by $\mu^{(H)} = R\sigma$ in the extrinsic range (only electrons or only holes). If both electrons and holes are present, the expressions for the Hall coefficient and the conductivity become

$$R = \frac{-n\mu_e^2 + p\mu_h^2}{(n\mu_e + p\mu_h)^2} \frac{3\pi}{8ec}$$

and

$$\sigma = e(n\mu_e + p\mu_h)$$

when scattering is by acoustical modes.

For intrinsic conduction $n = p$. The diffusion constants D_e and D_h for electrons and holes are related to the mobilities μ_e and μ_h by the *Einstein relation:*

$$D = \frac{kT}{e}\mu$$

The magnitude and temperature dependence of the mobility depend on the scattering mechanism. On the basis of a simplified theoretical model the temperature dependence is as follows:

Acoustical lattice scattering $\mu \sim T^{-\frac{3}{2}}$
Optical lattice scattering $\mu \sim (e^{\theta_L/T} - 1)$
Ionized impurity scattering $\mu \sim T^{\frac{3}{2}}$
Neutral impurity scattering $\mu \sim$ temperature-independent
Scattering by (edge) dislocations $\mu \sim T$

For details see ref. 1 and 3.

In reality the temperature dependence often deviates from the above proportionalities. The drift mobilities for Ge and Si in the lattice scattering range are given by (ref. 2)

Ge: $\mu_e^{(D)} = 4.90 \times 10^7 T^{-1.66}$ (100 K < T < 280 K)
$\mu_h^{(D)} = 1.05 \times 10^9 T^{-2.33}$ (100 K < T < 290 K)
Si: $\mu_e^{(D)} = 4.0 \times 10^9 T^{-2.6}$
$\mu_h^{(D)} = 2.5 \times 10^8 T^{-2.3}$

The Hall mobilities at room temperatures are (ref. 3)

Ge: $\mu_e^{(H)} = 4{,}500$ cm²/volt-sec
$\mu_h^{(H)} = 3{,}500$ cm²/volt-sec
Si: $\mu_e^{(H)} = 1{,}300$ cm²/volt-sec
$\mu_h^{(H)} = 500$ cm²/volt-sec

The $R\sigma$ product and the drift mobility of holes in germanium differ considerably; this is because of a small percentage of "fast" holes.

Hall mobilities of other semiconductors are listed in Tables 9e-1 and 9e-2.

References

1. Blatt, F. J.: *Solid State Phys.* **4**, 199 (1957).
2. Geballe, T. H.: "Semiconductors," p. 349, N. B. Hannay, ed., Reinhold Publishing Corporation, New York, 1959.
3. Putley, E. H.: "The Hall Effect and Related Phenomena," Butterworth & Co. (Publishers), Ltd., London, 1960.

9e-4. Thermoelectric Power. The thermoelectric power of semiconductors Q [measured in (micro) volts per degree] depends on the temperature, the number of carriers, the statistics, and the scattering mechanism. Some of the most common formulas (neglecting phonon-drag effects, ref. 2) are given below:

Extrinsic Range (one type of isotropic carriers, classical statistics, ref. 1):

$$Q = \pm \frac{k}{e}\left(r + \frac{\mathcal{E}_F}{kT}\right) = \pm \frac{k}{e}\left[r - \ln \frac{nh^3}{2(2\pi m^{(N)}kT)^{\frac{3}{2}}}\right]$$

where + refers to p-type, − to n-type semiconductors.

r = 2 for acoustical lattice scattering

r = 4 for ionized impurity scattering [actually (ref. 2) $r = 3.2$]

r = 3 for polar scattering

r = 2.5 for neutral impurity scattering

n = concentration of carriers, cm^{-3}

$m^{(N)}$ = density-of-states effective mass

$\mathcal{E}_F$ = Fermi energy measured from bottom of conduction band or top of valence band (positive in both cases), eV

k = Boltzmann constant, eV/deg

Transition Range (electrons and holes, classical statistics, ref. 1):

$$Q = -\frac{k}{e(nc+p)}\left[r(nc-p) - nc\ln\frac{nh^3}{2(2\pi m_e^{(N)}kT)^{\frac{3}{2}}} + p\ln\frac{ph^3}{2(2\pi m_h^{(N)}kT)^{\frac{3}{2}}}\right]$$

where n = concentration of electrons

p = concentration of holes

c = mobility ratio = μ_e/μ_h

Intrinsic Range (classical statistics, ref. 1):

$$Q = -\frac{k}{e}\frac{c-1}{c+1}\left(\frac{\mathcal{E}_g}{2kT} + r + \frac{3}{4}\frac{c+1}{c-1}\ln\frac{m_e^{(N)}}{m_h^{(N)}}\right)$$

where $\mathcal{E}_g = \mathcal{E}_0 + aT$ is the energy gap at temperature T.

A typical example of the temperature dependence of the thermoelectric power in n- and p-type semiconductors is shown in Fig. 9e-3. Phonon drag effects appear at lower temperatures.

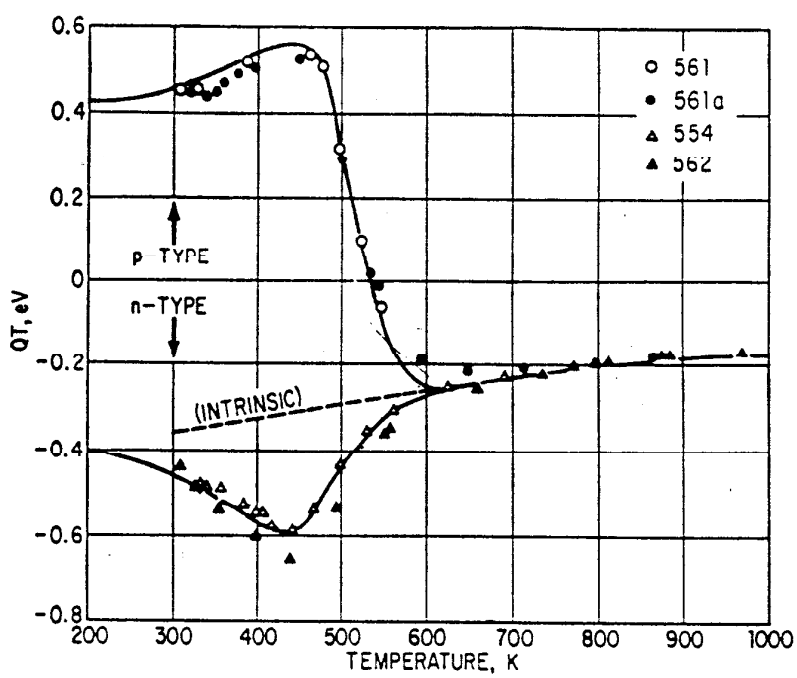

FIG. 9e-3. The thermoelectric power of silicon. Measured points and calculated curves for samples containing 8×10^{14} excess boron atoms per cm^3 (p-type) and 3×10^{14} excess phosphorus atoms per cm^3 (n-type). [*After Geballe and Hull, Phys. Rev.* **98**, 940 (1955).]

References

1. Johnson, V. A.: "Progress in Semiconductors," vol. I, p. 63, A. F. Gibson, ed., John Wiley & Sons, Inc., New York, 1956.
2. Herring, C.: *Phys. Rev.* **96**, 1163 (1954).

9e-5. Thermal Conductivity of Semiconductors. Values of the thermal conductivity for a few semiconductors are listed in Table 9e-4.

TABLE 9e-4. THERMAL CONDUCTIVITY OF SEMICONDUCTORS AT 300 K

	κ_L, watts/cm deg	Ref.		κ_L, watts/cm deg	Ref.
Diamond	1.51	1	AlP	0.8	2
Si	1.412	2	Te	0.063	1
Ge	0.606	2	PbS	0.024	3
InSb	0.166	2	PbSe	0.017	3
InAs	0.273	2	PbTe	0.022	3
InP	0.680	2	CdS	0.16	4
GaSb	0.390	2	As_2Te_3	0.025	3
GaAs	0.455	2	Bi_2Te_3	0.025	3
GaP	0.77	2	Mg_2Sn	0.10	3
AlSb	0.57	2	TiO_2 (c axis)	~0.10	5
AlAs	0.9	2			

References for Table 9e-4

1. Winkler, U.: *Helv. Phys. Acta* **28**, 633 (1955).
2. Willardson, R. K., and A. C. Beer, eds.: "Semiconductors and Semimetals," vol. 2, p. 3, Academic Press, Inc., New York, 1966–1968.
3. Aigrain, P., and M. Balkanski, eds.: "Selected Constants of Semiconductors," Pergamon Press, New York, 1961.
4. "American Institute of Physics Handbook," 2d ed., p. 4–94, McGraw-Hill Book Company, New York, 1963.
5. Thurber, W. R., and A. J. H. Mante: *Phys. Rev.* **139**, A1655 (1965).

9e-6. Impurities in Semiconductors. Purification of semiconductors by zone melting or by pulling a crystal from the melt is based on the fact that in most cases impurities tend to stay in the liquid rather than go into the solid. The essential parameter in this process is the *distribution coefficient* k, defined as the ratio of the concentrations of the impurity in the solid to that in the liquid host material. Distribution coefficients of certain elements in Si and Ge are compiled in Table 9e-5; these

TABLE 9e-5. DISTRIBUTION COEFFICIENTS IN SI AND GE†

Element	k (in Si)	k (in Ge)
Cu	.....	1.5×10^{-5}
Ag	.....	10^{-4}–10^{-6}
Au	3×10^{-5}	3×10^{-5}
Zn	.....	10^{-2}
B	6.8×10^{-1}	~20
Al	1.6×10^{-3}	10^{-1}
Ga	4×10^{-3}	10^{-1}
In	3×10^{-4}	1.1×10^{-3}
Tl	.....	4×10^{-5}
P	4×10^{-2}	1.2×10^{-1}
As	7×10^{-2}	4×10^{-2}
Sb	1.8×10^{-2}	3×10^{-3}
Fe	.....	2×10^{-6}
Co	.....	2×10^{-6}
Ni	.....	5×10^{-6}
Pt	10^{-5}	2×10^{-6}

† From W. Crawford Dunlap, "Introduction to Semiconductors," John Wiley & Sons, Inc., New York, 1957. (Dunlap uses for k the term segregation coefficient S.)

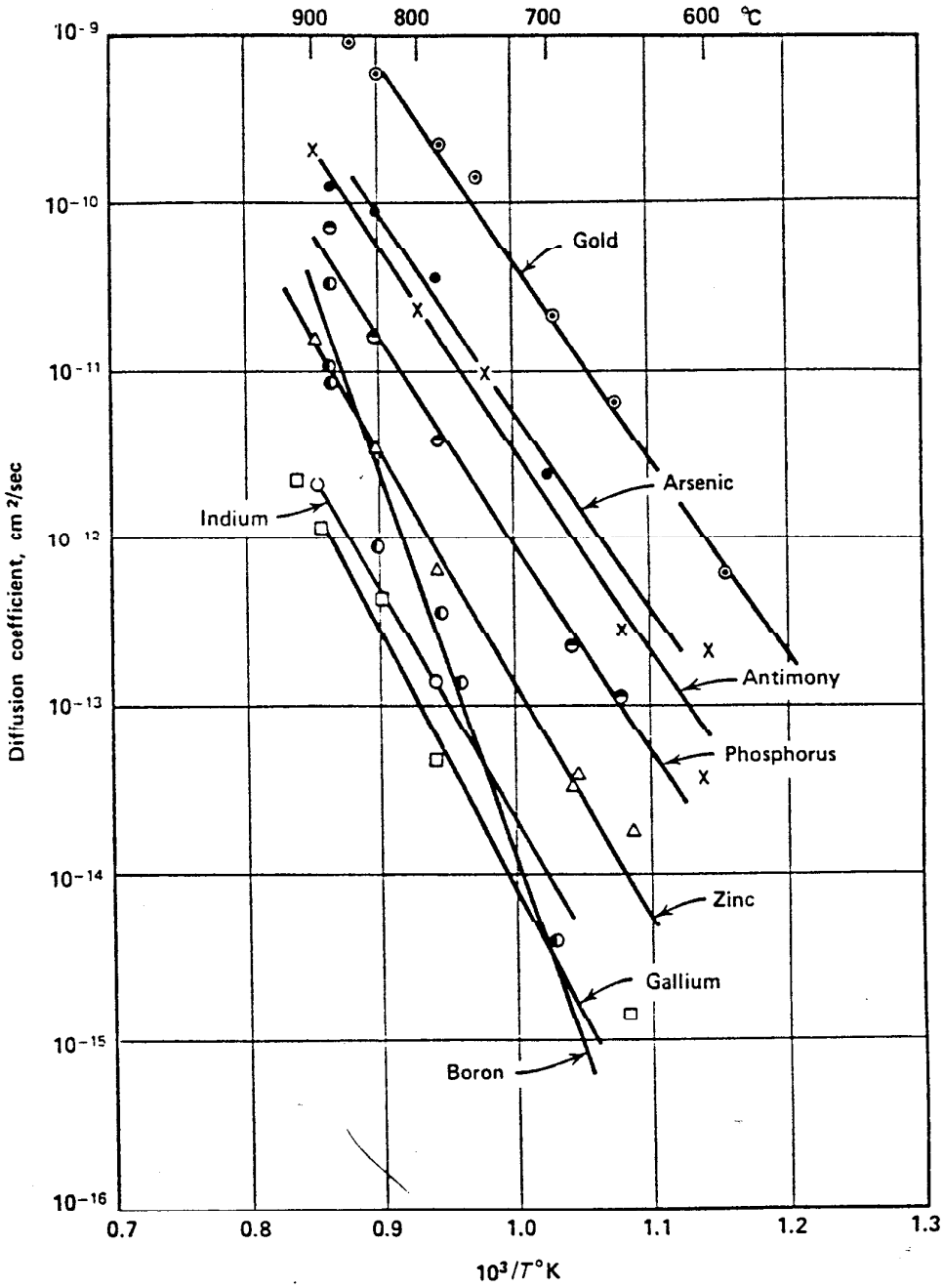

FIG. 9e-4. Diffusion coefficients of some impurities into germanium. (*After W. Crawford Dunlap, Jr., "An Introduction to Semi-conductors," p. 252, John Wiley & Sons, Inc., New York*, 1957.)

values refer to small impurity concentrations and equilibrium conditions (i.e., negligibly small gradients of concentration and temperature in the system).

Diffusion Coefficient. The "doping" of semiconductors as well as the preparation of *p-n* barriers depends greatly on the rate of diffusion. Extensive information exists about the diffusion coefficient D of impurities in Si and Ge. For other materials the data are scant. Approximate values of D are given in Figs. 9e-4 and 9e-5 and Table 9e-6. The magnitude of D depends somewhat on crystal perfection and

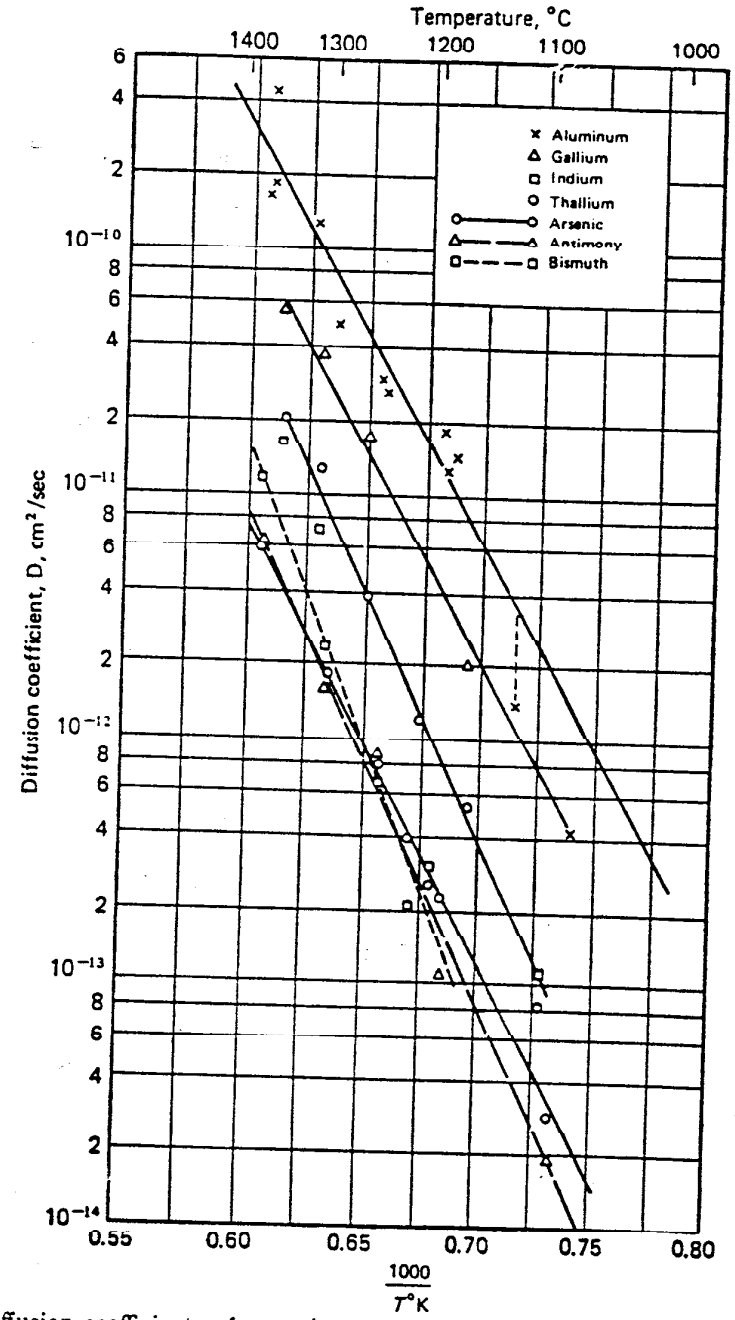

FIG. 9e-5. Diffusion coefficients of some impurities into silicon. [*After Fuller and Ditzenburger, J. Appl. Phys.* **27**, 544 (1956).]

impurity content. The activation energies of diffusion are usually of the order of a few tenths to a few electron volts.

Activation Energies of Carriers from Donors and Acceptors. Chemical additives or physical imperfections (vacancies, interstitials, dislocations) create localized energy states which can release or capture (trap) free carriers. The locations of these energy levels for certain impurities in Si and Ge are indicated in Figs. 9e-6 and 9e-7. The activation energies are given for low concentrations of impurities; at high concentration the activation energies decrease.

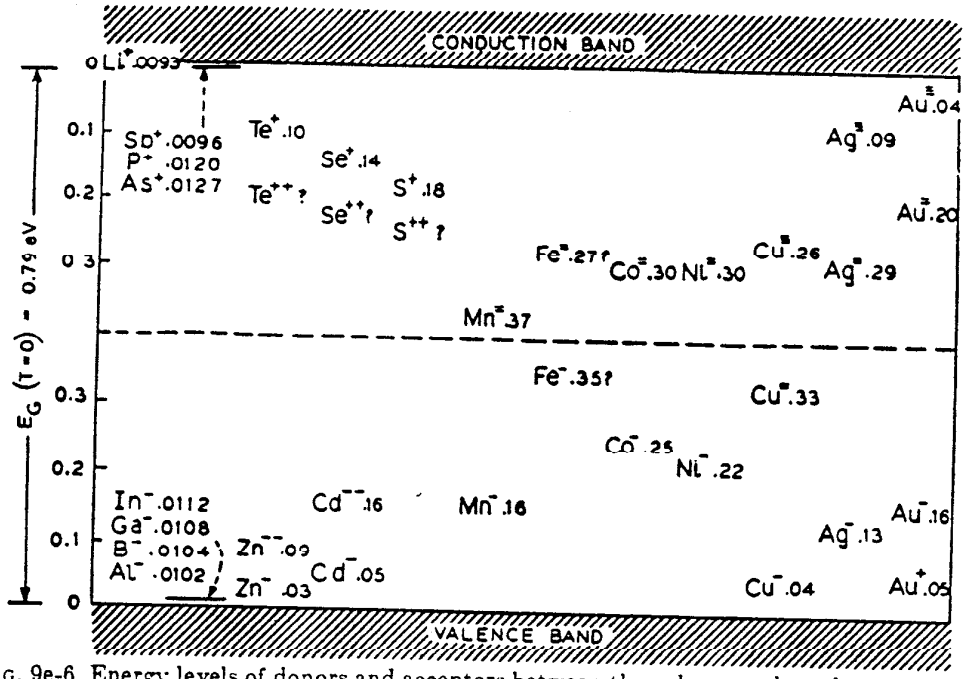

FIG. 9e-6. Energy levels of donors and acceptors between the valence and conduction bands of Ge. The ionization energy indicated (in eV) is required to produce what is presumed to be the ionic state shown and is measured from the nearest band edge, i.e., from the conduction band in the upper half of the diagram and from the valence band in the lower half. (*After T. H. Geballe, "Semiconductors," chap. 8, N. B. Hannay, ed., Reinhold Publishing Corporation, New York,* 1959.)

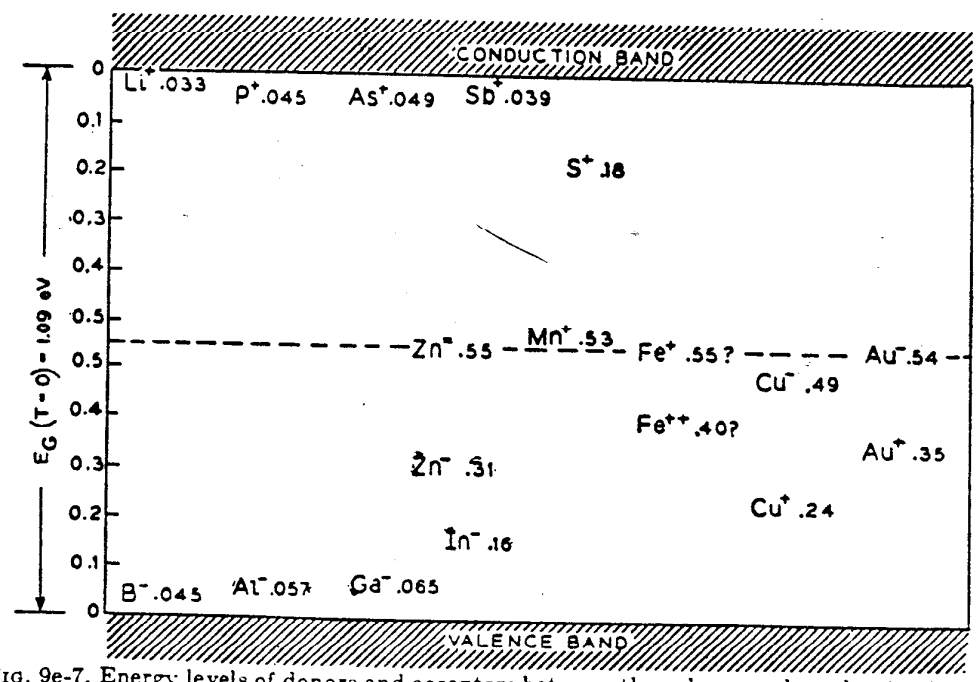

FIG. 9e-7. Energy levels of donors and acceptors between the valence and conduction bands of Si. (*After T. H. Geballe, "Semiconductors," chap. 8, N. B. Hannay, ed., Reinhold Publishing Corporation, New York,* 1959.)

TABLE 9e-6. DIFFUSION COEFFICIENTS AT TEMPERATURE T†

	D, cm²/sec	T, K
H in Si	2.4×10^{-4}	1500
He in Si	2.6×10^{-5}	1500
He in Ge	4×10^{-6}	1100
Li in Si	1.3×10^{-5}	1500
Li in Ge	1.3×10^{-5}	1100
Cu in Si	10^{-5}	1500
Cu in Ge	10^{-5}	1100
Cu in PbS	6×10^{-5}	800
Ni in Ge	10^{-5}	1100
Ni in PbS	2×10^{-5}	800
Fe in Si	1×10^{-6}	1500
Fe in Ge	2×10^{-6}	1100

† Sources: H. Reiss and C. S. Fuller, "Semiconductors," pp. 234, 244, N. B. Hannay, ed., Reinhold Publishing Corporation, New York, 1959; D. G. Thomas, "Semiconductors," pp. 289–290, N. B. Hannay, ed., Reinhold Publishing Corporation, New York, 1959.

Data on several impurity levels in other semiconductors are given in Table 9e-7.

TABLE 9e-7. ACTIVATION ENERGY OF IMPURITIES IN SEVERAL SEMICONDUCTORS

	Donor	$\mathcal{E}_d$, eV	Acceptor	$\mathcal{E}_a$, eV	Ref.
α-Sn	Sb	0.004	Mg	0.001	1
			Al	0.005	1
InSb	Te	<0.001	Zn	0.007	2
GaSb	.....	.....	Zn	0.024	3
AlSb	Te	0.068	...	.....	4
	Se	0.16	...	.....	4
GdS	Cl, Ga, S-vacancy	0.03	...	.....	5
PbS	Cu	0.02	...	.....	5
	Ni	0.03	...	.....	6
ZnO	H, Zn (Interst.)	0.05	...	.....	7
SiC	N	0.085	Al	0.275	8

References for Table 9e-7

1. Busch, G., and E. Mooser: *Helv. Phys. Acta* **26**, 611, 697 (1953).
2. H. Hrostowski et al.: *Phys. Rev.* 100, 1672 (1955).
3. Welker, H.: *Physica* **20**, 893 (1954).
4. Turner, W. J., and W. E. Reese: *Phys. Rev.* **117**, 1003 (1960).
5. Kröger et al.: *Z. Physik. Chem.* **203**, 1 (1954).
6. Scanlon, W. W.: *Solid State Phys.* **9**, 124 (1959).
7. Hutson, A. R.: "Semiconductors," p. 582, N. B. Hannay, ed., Reinhold Publishing Corporation, New York, 1959.
8. Lely, J. A., and F. A. Kröger: "Halbleiter und Phosphore," p. 525, Schön and Welker, eds., Friedrich Vieweg und Sohn, Brunswick, Germany, 1958.

9e-7. Charge-carrier Lifetime. Several mechanisms affect the lifetime of charge carriers in semiconductors.

1. Direct recombination of an electron in the conduction band with a hole in the valence band. The radiative recombination lifetime τ_r associated with this process is given by

$$\tau_r = \frac{n_i}{2R}$$

where n_i is the intrinsic carrier concentration and R is the rate of radiative recombination.[1]

2. Indirect recombination (via recombination centers). The electron (hole) is captured by an impurity center, which subsequently captures a hole (electron). In most semiconductors the lifetime is limited by this process. The impurity centers can be either volume or surface states.

3. Auger process. An electron recombines with a hole, and the emitted energy is absorbed by a third carrier.

4. Trapping process. An electron (hole) is captured by a center (trap) but is thermally reexcited into the conduction (valence) band before it can recombine with a hole (electron). Surface states often act as traps.

Except for direct recombination, lifetimes pertain to electrons *or* holes. The minority-carrier lifetimes can also be expressed in terms of the capture cross sections of a center (A_n for electron capture by empty centers and A_p for hole capture by filled centers). The lifetime and the cross section are related by the following expression:

$$\tau_{n,p} = \frac{1}{N_t \langle v A_{n,p} \rangle}$$

where N_t is the density of centers and v is the thermal velocity of electrons or holes.

Data on some observed lifetimes τ_o and calculated radiative lifetimes τ_c at 300 K are listed in Table 9e-8.

TABLE 9e-8. CARRIER LIFETIMES

	τ_o, sec*	τ_c, sec	Ref.
Ge	10^{-2}	0.3	1
Si	10^{-4}	3.5	1
PbS	20×10^{-6}	63×10^{-6}	2
PbSe	.....	80×10^{-6}	2
PbTe	.....	6.8×10^{-6}	2
GaAs	$\tau_{maj} > 10^{-6}$	.....	3
	$\tau_{min} \ll 10^{-6}$		3
GaSb	10^{-6}	.....	3
InP	$\tau_e \approx 10^{-6}$	.....	3
	$\tau_h \approx 2 \times 10^{-3}$		3
InAs	$10^{-7} - 10^{-8}$	.....	3
InSb	10^{-7}	.....	3

* Largest values observed in single crystals. Films or specially treated samples may show much longer, or much shorter, "effective" lifetimes.

References for Table 9e-8

1. Petritz, R. L.: In "Photoconductivity Conference," p. 62, R. G. Breckenridge et al., eds., John Wiley & Sons, Inc., New York, 1956.
2. Scanlon, W. W.: *Solid State Phys.* **9**, 117, 136 (1959).
3. Willardson, R. K., and A. C. Beer, eds.: "Semiconductors and Semimetals," vol. 2, p. 205, Academic Press, Inc., New York, 1966–1968.

9e-8. Lattice Properties. Most semiconductors show an optical absorption and an anomalous dispersion in the far-infrared region. This effect is rather small in covalent semiconductors like Ge and Si; it increases, however, with increasing polar character. On the basis of an expression derived by Born and Huang (ref. 1) it is possible to calculate an *effective charge* e^* which describes the deviation from homo-

[1] W. Van Roosbroeck and W. Shockley, *Phys. Rev.* **94**, 1558 (1954).

polarity. The optical lattice vibrations are divided into transverse and longitudinal modes with frequencies ω_T and ω_L.

The acoustical lattice vibrations are related to the *elastic constants* C_{lm}; these modes also determine the lattice specific heat, which is described by the *Debye temperature* θ. The phonon dispersion (frequency ω vs. wave vector q) has been measured for a number of cubic crystals, using the technique of inelastic neutron scattering (ref. 2). An example (Ge) is shown in Fig. 9e-8.

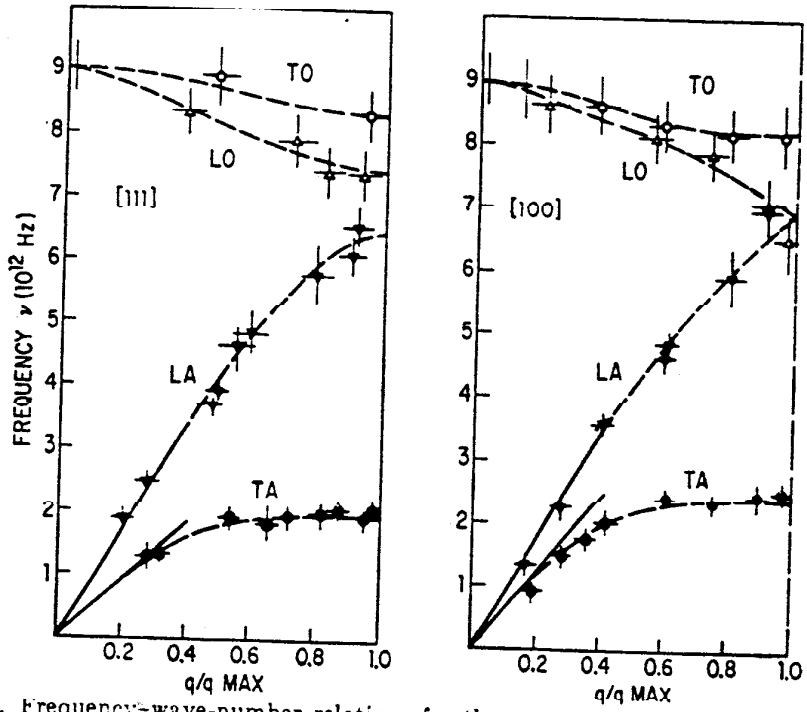

FIG. 9e-8. Frequency-wave-number relations for the <100> <111> directions in germanium. [*After Brockhouse and Iyengar, J. Phys. Chem. Solids* **8**, 400 1959.]

Data on ω_T, ω_L, ϵ^*, θ_0, and elastic constants for a number of semiconductors are assembled in Table 9e-9.

References

1. Born, M., and V. Huang: "Dynamical Theory of Lattices," p. 114, Oxford University Press, New York, 1954.
2. Brockhouse, B. N., and P. K. Iyengar: *Phys. Rev.* **111**, 747 (1958).

9e-9. Refractive Index and Dielectric Constant. The *dielectric constant* in ionic lattices depends on frequency. Neglecting dissipative forces this dependence is given by

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_{st} - \epsilon_\infty}{1 - (\omega/\omega_T)^2}$$

where ω_T is the lattice vibration frequency for long-wavelength transverse waves. For high frequencies $\omega \gg \omega_T$: $\epsilon = \epsilon_\infty$, the optical dielectric constant; for low frequencies $\epsilon = \epsilon_{st}$, the static dielectric constant.

The optical dielectric constant is related to the *refractive index* by the following expression:

$$n^2 = \epsilon_\infty$$

For nonpolar materials $\epsilon_{st} = \epsilon_\infty$. The dielectric constants of Ge and Si are 16 and 11.8, respectively. Values of n and ϵ_{st} for other semiconductors are given in Table 9e-9.

TABLE 9c-9. LATTICE PROPERTIES OF SEMICONDUCTORS

	ω_T, cm^{-1}	ω_L, cm^{-1}	Ref.	10^{11} N/m^2 at 300 K			θ	Ref.	ϵ_s	n	e^*	Ref.
				C_{11}	C_{12}	C_{44}						
Diamond	1,333	.....	1*a*	10.76	1.25	5.76	2240	1*c*	5.5	2.4	0	1*d*
Si	518	.....	1*a*	1.656	0.639	0.796	645	4	11.7	3.44	0	1*d*
Ge	309	.....	1*a*	1.288	0.483	0.671	374	4	15.8	3.97	0	1*d*
InSb	180	191.3	1*b*	0.672	0.367	0.302	203	3	17.88	3.96	0.42	2
InAs	218.9	243.3	1*b*	0.833	0.453	0.396	247	3	14.55	3.44	0.56	2
InP	303.7	345	1*b*	.....	.....	.....	321	3	12.37	3.1	0.66	2
GaSb	230.5	240.3	1*b*	0.885	0.404	0.433	266	3	15.69	3.8	0.33	2
GaAs	268.2	290.5	1*b*	1.188	0.538	0.594	344	3	13.13	3.3	0.51	2
GaP	366.3	401.9	1*b*	.....	.....	.....	.....	3	10.18	2.9	0.58	2
AlSb	318.8	339.6	1*b*	0.894	0.442	0.415	292	3	11.2	3.14	0.48	2
BN	820	835	1*b*	.....	.....	.....	.....	.....	7.1	2.1	1.14	2
ZnS(Z)	339	298	6*a*	1.046	0.653	0.461	315	6*b*	8.3	2.24	0.48	5
CdS(W)	261	295	6*a*	0.907	0.581	0.150	.....	6*b*	ϵ_{11} = 9.4, ϵ_{33} = 10.3	2.29	....	6*a*
	238	.....	...	C_{13} = 0.510	C_{33} = 0.938							
PbS	65	223	9	1.27	0.298	0.248	227	11, 14	205	17.4	....	8
				1.02	0.38	0.25	.....	12				
PbSe	.....	44	8	.....	.....	.....	138	14	280	23.6	....	8
PbTe	31	110	10	1.08	0.077	0.134	125	13, 14	400	5.63	0.55	5
TiO_2	125–167	360–400	15	0.273	0.176	0.125	~758	16	173 (*c*)	.....	....	15
	400–533	770–823		C_{13} = 0.149	C_{13} = 0.484	C_{66} = 0.194	.....	.....	89 (*a*)			

References for Table 9e-9

1*a*. Cowley, R. A.: *Proc. Phys. Soc. (London)* **88**(*II*), 463 (1966).
1*b*. Hass, Marvin: in "Semiconductors and Semimetals," vol. 1, p. 7, R. K. Willardson and A. C. Beer, eds., Academic Press, Inc., New York, 1966–1968.
1*c*. McSkimin, H. J., and W. L. Bond: *Phys. Rev.* **105**, 116 (1957).
1*d*. Aigrain, P., and M. Balkanski, eds.: "Selected Constants of Semiconductors," Pergamon Press, New York, 1961.
2. Hass, Marvin: In "Semiconductors and Semimetals," vol. 1, p. 14, R. K. Willardson and A. C. Beer, eds., Academic Press, Inc., New York, 1966.
3. Drabble, J. R.: in "Semiconductors and Semimetals," vol. 2, p. 110, R. K. Willardson and A. C. Beer, eds., Academic Press, Inc., New York, 1967.
4. McSkimin, H. J.: *J. Appl. Phys.* **24**, 988 (1953).
5. Burstein, E.: In "Lattice Vibrations," p. 315, R. Wallis, ed., Pergamon Press, New York, 1965.
6*a*. Reynolds, D. C., et al.: *Phys. Stat. Solidi* **12**, 3 (1965).
6*b*. Berlincourt, D., et al.: *Phys. Rev.* **129**, 1009 (1963).
7. Zemel, J. N., et al.: *Phys. Rev.* **140**, A330 (1965).
8. Burstein, E., et al.: "Proceedings of the International Conference on the Physics of Semiconductors," p. 1065, M. Hulin, ed., Dunod, Paris, 1964.
9. Elcombe, M. M.: *Proc. Roy. Soc. (London)*, ser. A, **300**, 210 (1967).
10. Cochran, W., et al.: *Proc. Roy. Soc. (London)* ser. A, **293**, 433 (1966).
11. Bhagavantam, S., and T. S. Rao: *Nature* **168**, 42 (1951).
12. Ramachandran, G. N., and N. A. Wooster: *Acta Cryst.* **4**, 335 (1951).
13. Houston, B., et al.: *J. Appl. Phys.* **39**, 3913 (1968).
14. Parkinson, D. H., and J. E. Quarrington: *Proc. Phys. Soc. (London)*, ser. A, **67**, 569 (1954).
15. Cronemeyer, D. C.: *Phys. Rev.* **112**, 800 (1958).
16. Values corrected by F. Birch from work by Verma, R. K.: *J. Geophys. Res.* **65**, 757 (1960).