Intervalley-Scattering Selection Rules in III-V Semiconductors

JOSEPH L. BIRMAN*
New York University, University Heights, New York, New York
AND
MELVIN LAX
Bell Telephone Laboratories, Murray Hill, New Jersey
AND
RODNEY LOUDON†
Royal Radar Establishment, Malvern, England

(Received 6 October 1965)

Selection rules are presented for intervalley scattering between the lowest conduction-band minima at Γ, X, and L in the Brillouin zone of a III-V semiconductor. These selection rules are required for theories of the Gunn effect. The two most important crystals experimentally are GaAs, where longitudinal optic phonons cause the intervalley scattering, and InP, where longitudinal acoustic phonons produce the scattering.

THE selection rules for intervalley-scattering processes in III–V semiconductors are important in theories of the Gunn effect.[1] This type of selection rule has been calculated by a variety of methods, using either the full space group of the crystal lattice[2] or an appropriate subgroup of the crystal space group.[3–6] The underlying group-theoretical manipulations are straightforward to carry out, and indeed the required decompositions of direct products of irreducible representations are contained in some extensive tabulations published a while ago.[2] However, the selection-rule calculation requires additionally a knowledge of the symmetry characters of the phonons and electronic states involved in the intervalley scattering. We supply this information in the present paper and display the selection rules explicitly. The rules have been checked by obtaining the same results by the full-space-group and subgroup methods. Our results supply the definite answer to a controversy which arose at the Princeton Solid State Device Research Conference in 1965 concerning the phonons allowed to participate in intervalley scattering in GaAs.

The III–V semiconductors have cubic-zinc-blende structure with space group T_d^2. The character tables have been presented by Parmenter[7] and Dresselhaus,[8] and we use their notation for the irreducible representations. The main features of the energy bands are known experimentally for many of the III–V semiconductors,[9] and the energy-band theory for some of these compounds has been given by Bassani and Yoshimine.[10] The Gunn effect apparently occurs in crystals where the lowest conduction-band minimum lies at the center of the Brillouin zone. The favored explanation of the effect[1] envisages a process in which electrons close to the conduction-band minimum are scattered by phonons to higher conduction-band minima where the electron mobility is smaller. We therefore require the selection rules for scattering from the lowest conduction-band minimum to higher minima. Electron scattering between degenerate conduction-band minima at similar points in the Brillouin zone is also important in determining the thermal equilibrium state of the crystal.

Experiment[9] shows that the lowest conduction band at $\Gamma(000)$ has Γ_1 symmetry. The higher minima may occur at $X(1,0,0)2\pi/a$ or $L(\frac{1}{2},\frac{1}{2},\frac{1}{2})2\pi/a$ points in the zone. The positions of the lowest and second lowest conduction-band minima in the III–V semiconductors are listed in Table I, which uses information collected in Ref. 9. The theory[10] predicts two bands close together at X having symmetries X_1 and X_3. Let us choose the origin of coordinates for the space-group operations to be at a group-V atom (this is consistent with the notation adopted by Bassani, Ref. 10 and private com-

* Partially supported by the U. S. Army Research Office (Durham) and the Aerospace Research Laboratories, Office of Aerospace Research, Wright-Patterson Air Force Base, Ohio.

† Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.

[1] E. Conwell (private communication); P. N. Butcher and W. Fawcett, Proc. Phys. Soc. (London) **86**, 1205 (1965).

[2] J. L. Birman, Phys. Rev. **127**, 1093 (1962).

[3] R. J. Elliott and R. Loudon, J. Phys. Chem. Solids **15**, 146 (1960).

[4] M. Lax and J. J. Hopfield, Phys. Rev. **124**, 115 (1961).

[5] M. Lax, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and The Physical Society, London, 1962), p. 395.

[6] M. Lax, Phys. Rev. **138**, A793 (1965).

[7] R. H. Parmenter, Phys. Rev. **100**, 573 (1955). Note that W_3 and W_4 are incorrectly quoted as time-reversal degenerate in this reference. Note that Parmenter has chosen Γ_{15} to transform as (x,y,z). Thus Parmenter's Γ_{15} (and Dresselhaus' Γ_4) have odd-parity basis functions that are identical to those for $\Gamma_{15}^-=\Gamma_4^-$ of the group O_h. But the even-parity basis functions for Γ_{15} in T_d will then correspond to those of $\Gamma_{25}^+=\Gamma_5^+$ in O_h. To make the more logical choice of requiring even-parity representations in O, T_d and O_h to agree interchanges the names Γ_{15} and Γ_{25} in T_d. This is done for example, by G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz in *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, Massachusetts, 1963).

[8] G. Dresselhaus, Phys. Rev. **100**, 580 (1955).

[9] C. Hilsum, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 1127.

[10] F. Bassani and M. Yoshimine, Phys. Rev. **130**, 20 (1963).

TABLE I. Positions of the lowest and second lowest conduction-band minima in the III–V semiconductors.

	Material								
	GaSb	GaAs	GaP	AlSb	AlAs	AlP	InSb	InAs	InP
1st minimum	Γ	Γ	X	X	X	X	Γ	Γ	Γ
2nd minimum	L	X	L	L	L or Γ	Γ	L	L	X

munication). To see that the X_1 state should have a lower energy than the X_3 state, we are indebted to Phillips,[11] who remarked that the group-V atom with a partially screened charge of 5 is more attractive than the group-III atom with a partially screened charge of 3. The X_1 state is even under the twofold rotations about the two orthogonal axes perpendicular to ΓX, whereas the X_3 state is odd under these rotations. Thus the X_1 electron has s-like character at the group-V atom, while the X_3 electron is p-like and vanishes at the group-V nucleus. The s- and p-like characters are reversed at the group-III atomic site. Since the X_1 electron concentrates its charge at the more attractive site, it is more strongly bound than the X_3 electron. The higher minima may also lie at L points in the Brillouin zone, where the lowest band is presumed to have L_1 symmetry.[10]

For the scattering between different types of valley we require the following Kronecker products of space-group representations

$$\begin{aligned} &\Gamma_1 \times X_1 = X_1, \\ &\Gamma_1 \times L_1 = L_1, \\ &L_1 \times X_1 = L_1 + L_3. \end{aligned} \tag{1}$$

These results can be calculated by any of the standard methods.[2–6] For scattering within or between valleys of the same symmetry type (i.e., valleys belonging to the same star), the ordinary Kronecker products of the irreducible representations of the electron wave functions must be replaced by the symmetric Kronecker products.[5] For scattering within the same valley the decompositions are

$$\begin{aligned} &[\Gamma_1]_{(2)} = \Gamma_1, \\ &[X_1]_{(2)} = \Gamma_1 + \Gamma_{12}, \\ &[L_1]_{(2)} = \Gamma_1 + \Gamma_{15}, \end{aligned} \tag{2}$$

while scattering between different valleys of the same symmetry type requires

$$\begin{aligned} &[X_1]_{(2)} = X_1, \\ &[L_1]_{(2)} = X_1 + X_3. \end{aligned} \tag{3}$$

Additional ordinary and symmetric Kronecker products of this type can be found in the tabulation by Birman.[2]

The irreducible representations listed on the right-hand sides of (1), (2) and (3) show the symmetries of phonons which can cause the transition of an electron between the states whose symmetries are listed on the left-hand sides. The phonon symmetries in the zinc-blende crystal structure are as follows[12]

$$\begin{aligned} &\Gamma\colon \Gamma_{15}(\text{optic}) + \Gamma_{15}(\text{acoustic}) \\ &X\colon X_5(\text{TO}) + X_1(\text{LO or LA}) \\ &\qquad + X_3(\text{LA or LO}) + X_5(\text{TA}), \\ &L\colon L_3(\text{TO}) + L_1(\text{LO}) + L_1(\text{LA}) + L_3(\text{TA}). \end{aligned} \tag{4}$$

The ambiguity concerning the symmetries of the longitudinal phonons at X is due to the dependence of the character of the phonons on the relative magnitudes of the masses of the group-III and group-V atoms. Since X_1 is a mode in which the atom at the origin (the V atom) stands still, if the group-V atom is the heavier, we would expect X_1 to have the higher frequency (longitudinal optic, LO) and X_3 to have the lower frequency (longitudinal acoustic, LA).[13] These symmetries are interchanged if the group-III atom is the heavier. It is, of course, essential to use the same origin in classifying the phonons as in classifying the electrons. We use the group-V atom as origin throughout; a change to the group-III atom as origin would interchange X_1 and X_3. This example makes it clear that whenever irreducible representations are quoted, the origin of coordinates should be stated (in addition to the standard wave vector $\mathbf{k}$ to which the representation is referred).

Combining (1) and (4), we can write down the selection rules:

Electron transition:

$$\begin{aligned} &\Gamma_1 \to X_1, \text{ LO phonon if } M_V > M_{III}, \\ &\qquad\qquad \text{LA phonon if } M_V < M_{III}; \\ &\Gamma_1 \to L_1, \text{ LO and LA phonons}; \\ &L_1 \to X_1, \text{ all L phonons.} \end{aligned} \tag{5}$$

For scattering between different valleys belonging to the same star, (3) and (4) give

Electron transition:

$$\begin{aligned} &X_1 \to X_1, \text{ LO phonon if } M_V > M_{III}, \\ &\qquad\qquad \text{LA phonon if } M_V < M_{III}; \\ &L_1 \to L_1, \text{ LO and LA phonons.} \end{aligned}$$

Finally, for scattering within a valley we use Eqs. (2). These equations appear to show that intravalley scattering can occur only for the L_1 valley of the three cases considered. However, it is well known that the group-theoretical threefold degeneracy of the optic phonon at Γ is lifted by dipolar forces as soon as the phonon wave vector departs from zero.[14] The same

[11] J. C. Phillips (private communication).

[12] J. L. Birman, Phys. Rev. 131, 1489 (1963).

[13] This supposes, of course, that inequalities in III–III and V–V forces are small compared to the III–V forces.

[14] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), Secs. 7 and 8.

dipolar forces cause an electron-phonon interaction which allows the longitudinal optic phonon to produce intravalley scattering. The long-wavelength acoustic phonons can also cause intravalley scattering for small but finite phonon wave vectors. In this case the electron-phonon interaction is proportional to the strain produced by the phonon. The possible strains are Γ_1=pure dilatation and Γ_{12} and Γ_{15} which are both shears. Which of these strains cause scattering, in each valley, is given by the selection rules summarized in (2). Thus intravalley scattering is allowed for all three transitions in Eq. (2).

The two most fruitful III–V semiconductors for observation of the Gunn effect are GaAs and InP. Both have lowest conduction-band minima at Γ and next higher minima at X. For GaAs, the $\Gamma_1 \rightarrow X_1$ and $X_1 \rightarrow X_1$ electron transitions proceed by interaction with the LO phonon. For InP it is the LA phonon which produces the intervalley scattering.

If the higher valleys are not exactly at the points X in the Brillouin zone, but lie on the line Δ which runs from Γ to X, the selection rules become less restrictive. For any relative size of the atomic masses, both longitudinal phonons can cause scattering from Γ_1 to Δ_1. For scattering between adjacent valleys Δ_1, e.g., from $(k,0,0)$ to $(0,k,0)$, the allowed phonon symmetry is Σ_1; one of the transverse optic phonons, the LO and LA phonons, and one of the transverse acoustic phonons all have this symmetry. For transitions across the zone, e.g., from $\Delta_1(k,0,0)$ to $\Delta_1(-k, 0, 0)$, both the longitudinal phonons can cause scattering.

The full-space-group and subgroup methods predict the same selection rules for all the processes considered in this paper. Karavaev[15] has recently put forward the view that the subgroup methods may sometimes fail to provide the full selection rules for scattering processes in crystals. Our work shows that the subgroup methods do not suffer from any such deficiency as far as intervalley scattering in III–V semiconductors is concerned.

[15] G. F. Karavaev, Fiz. Tverd. Tela **6**, 3676 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2943 (1965)].

PHYSICAL REVIEW VOLUME 145, NUMBER 2 13 MAY 1966

Evidence for L Bands in NaCl†

ROBERTO FIESCHI*
Istituto di Fisica dell'Università di Parma, Parma, Italy
AND
PAOLA SCARAMELLI*
Istituto di Fisica dell'Università di Milano, Milano, Italy

(Received 29 December 1965)

NaCl crystals are investigated in the spectral range 200–800 mμ by means of photostimulated thermoluminescence and differential-absorption-spectrum measurements. Four weak bands are found on the high-energy side of the F band, which have the properties of L bands: weak absorption coefficient, high and temperature-independent ionization efficiency, ionization intensity roughly proportional to the concentration of F centers. Moreover, it is found that thermoluminescence is stimulated only by light absorbed by electron centers (R, F, K, L bands), not by V centers.

1. INTRODUCTION

SOME years ago, L bands were observed by Lüty in potassium and rubidium halides[1,2]; recently Klick gave some evidence on the presence of L bands in LiCl.[3] Although no detailed theoretical model had hitherto been worked out, there is convincing evidence now that the L bands are due to F-center transitions: (a) There is a good proportionality between the L and F band intensities; on the other hand, no relation is found between L bands and crystal purity. (b) The quantum efficiency of $F \rightarrow F'$ conversion under L light is ~ 2 (as under F light).[4] (c) By depopulating the F-center ground state with intense chopped F light, the L-band absorption also decreases, showing that the L bands are caused by transitions starting from the fundamental state of the F centers.[5] (d) Photoconductivity measurements[6,7] show that the quantum efficiency of the L bands is unity, indicating that they

† This research has been sponsored in part by the U. S. Air Force Office of Scientific Research under Grant AF EOAR 65-07 with the European office of Aerospace Research.

* Gruppo Italiano di Struttura della Materia (GNSM) of the Consiglio Nazionale delle Ricerche.

[1] F. Lüty, Z. Physik **160**, 1 (1960).
[2] F. Lüty, Halbleiterprobleme **4**, 238 (1961).
[3] C. C. Klick, Phys. Rev. **137**, A1814 (1965).
[4] M. Hunger and F. Lüty, Phys. Letters **15**, 114 (1965).
[5] G. Chiarotti and U. M. Grassano, in Symposium on Color Centers, Urbana, October, 1965 (unpublished).
[6] F. Nakasawa and H. Kanzaki, J. Phys. Soc. Japan **20**, 468 (1965).
[7] R. S. Krandall and M. Mikkor, Phys. Rev. **138**, A1247 (1965).