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Muonium in Silicon and Germanium—a Deep Donor

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The hyperfine splitting of muonium in Si and Ge is analyzed on various models of the dielectric properties of the medium. Muonium acts as a deep donor in Si and Ge, contrary to some earlier predictions. It is possible to give a reasonable account of the observed values of $|\psi(0)|^2$ in terms of the Reiss–Kaus cavity models, and in terms of the Walter–Cohen $\epsilon(q)$ calculated from the actual band structures, provided that the electron mass is taken as essentially equal to the free-electron mass. Identical results are expected for interstitial atomic hydrogen.

I. INTRODUCTION

Muonium, a hydrogenlike atom composed of an electron and a positive muon, is formed in solids when a muon comes to rest. The hyperfine splitting of muonium can be measured with considerable accuracy by studying the precession of the spin in a magnetic field. This precession is revealed by the direction of the positron emitted in the decay reaction $\mu^+ \rightarrow e^+ + \bar{\nu}_\mu + \nu_e$, with a lifetime of 2.2 μsec. From a Fourier analysis of the precession signal it is possible to obtain the value of the hyperfine splitting of the ground state of the muonium atom in the medium. From the observed hyperfine splitting and the contact hyperfine equation one finds an experimental value for $|\psi(0)|^2$, the probability density of the electron at the muon.

Such experiments were first carried out by Gurevich and co-workers.[1,2] They found, for example, that the hyperfine splitting of muonium in ice (4791 ± 300 MHz) and in fused quartz (4404 ± 70 MHz) are not far from the splitting in vacuum (4463 MHz) and lead to values of $|\psi(0)|^2$, consistent with values observed by EPR for atomic hydrogen in the same media.

The story is different for muonium in germanium and silicon. In germanium Gurevich and co-workers[2] at Dubna found

$$|\psi(0)|^2_{\mathrm{Ge}} / |\psi(0)|^2_{\mathrm{vac}} = 0.58 \pm 0.04 ,$$

and for silicon Crowe and co-workers[3] at Lawrence Berkeley Laboratory found

$$|\psi(0)|^2_{\mathrm{Si}} / |\psi(0)|^2_{\mathrm{vac}} = 0.444 \pm 0.020 .$$

It is seen from these values that the effects of the medium are important in Ge and Si as compared to ice and fused quartz. It is not possible at present to compare these values with those for atomic hydrogen in germanium and in silicon for the simple reason that the presence of atomic hydrogen in these crystals has never actually been detected by a direct physical measurement, to our knowledge.[4] We expect that the donor states will be identical for H as for muonium, so that the hyperfine splittings should be near 630 and 820 MHz, as compared with the vacuum splitting 1420 MHz.

It has been widely believed[5] that hydrogen may be the most common impurity in crystals of Ge and Si normally considered pure. In the un-ionized state the H or H_2 would not affect the electrical properties. It is known that Ge and Si are permeable to hydrogen at elevated temperatures,[6] and there is some hope that it can be quenched in these crystals by rapid cooling. (The criterion for successful quenching is essentially that the phonons should diffuse out of the crystal faster than the hydrogen.) However, at the moment of writing we know more about muonium in Ge and Si than about H or H_2 in just these crystals on which rests most of modern solid-state electronics technology. Unfortunately we do not know the ionization energy of either muonium or H in Ge or Si, so we have to draw our conclusions only from the experimental values of $|\psi(0)|^2$.

It was recognized a long time ago by Reiss[7] and Kaus[8] that the hydrogenic or Kittel–Mitchell–Luttinger–Kohn (KMLK)[9] or effective-mass approximation, which is used successfully for group-V donors in Ge and Si, will not apply to interstitial hydrogen. This is expected to be a deep donor rather than a shallow donor.[10] Both authors show that interstitial Li should be a shallow donor, in agreement with experiment. The decision between deep and shallow levels is essentially whether the state can be bound within the vacuumlike region near the interstitial core. It is easier to bind the 1s state of hydrogen (with zero nodes) than the 2s state of lithium (with one node), and so in hydrogen the ground state is deep. Just how deep is not known experimentally. If it were a shallow donor it should have been detected electrically by now. Hall measurements vs temperature can tell us whether a donor is shallow or deep, that is, thermally ionized at ordinary temperatures or not thermally ionized.

If muonium were a shallow donor the ionization energy would be about 30 meV in Si and 10 meV in Ge. The probability density $|\psi(0)|^2$ would scale as a/a_{H}^{*3} or as $(m^*/\epsilon)^3/a_{\mathrm{H}}^3$. Here a_{H}^* denotes the effective Bohr radius in the medium and a_{H} is the vacuum Bohr radius. On the shallow donor or effective-mass model the value of $|\psi(0)|^2$ would be reduced with respect to vacuum by a factor of $\sim 10^{-5}$ in Si and $\sim 10^{-7}$ in Ge, completely out of line with the experiments.

The theoretical problem depends critically on how we treat the immediate neighborhood of the interstitial muon. What we need to know to do the problem properly includes: (a) the position $\vec{\mathbf{X}}$ of the muon in the lattice; (b) the dielectric function $\epsilon(\omega, \vec{p}, \vec{\mathbf{X}})$ or $\epsilon(\omega, \vec{q}, \vec{q}')$; and (c) a method for treating the transition between the effective-mass tensor $m_{\alpha\beta}$ in the crystal and the free-electron mass m that must obtain close to the muon. In one approximation we say that we need to know $m_{\alpha\beta}(\vec{p}, \vec{\mathbf{X}})$. But in an exact treatment of the problem the Schrödinger equation will involve only m.

None of these quantities is known reliably. What we shall do is to extend several treatments, admittedly crude, used in the past and we shall see what has to be true to account for the muonium results. We first treat the cavity models. We then consider treatments with a wave-vector-dependent dielectric function $\epsilon(\vec{q})$. Both approaches lead to a reasonable magnitude for $|\psi(0)|^2$.

CAVITY MODELS

The static dielectric function at a distance r from the muon is assumed to have the asymptotic behavior $\epsilon(r) \to 1$ as $r \to 0$ and $\epsilon(r) \to \epsilon_0$ as $r \to \infty$. We might take $\epsilon = 1$ out to a cavity radius R and $\epsilon = \epsilon_0$ for $r > R$, but the resulting discontinuity in the potential at R is unphysical:

$$V_D(r) = \begin{cases} -e^2/r & \text{for } r < R \\ -e^2/\epsilon_0 r & \text{for } r > R\ . \end{cases} \tag{1}$$

The following potential has been used extensively[7,8,11] as a first attempt to take account of the r dependence of the dielectric function:

$$V_C(r) = \begin{cases} -e^2/r + e^2(1 - 1/\epsilon_0)/R & \text{for } r < R \\ -e^2/\epsilon_0 r & \text{for } r > R\ . \end{cases} \tag{2}$$

Now there is only a discontinuity in the electric field at R. The constant term in (2) has been discussed especially by Kaus,[8] who also took account of the effective mass in the spirit of the cavity model:

$$m(r) = \begin{cases} m & \text{for } r < R \\ m^* & \text{for } r > R\ . \end{cases} \tag{3}$$

Both Reiss and Kaus were able to explain why hydrogen does not ionize thermally in Si and Ge.

We have extended somewhat the calculations of Kaus. The ionization energy $-E$ is shown on a logarithmic scale in Fig. 1 as a function of the cav-

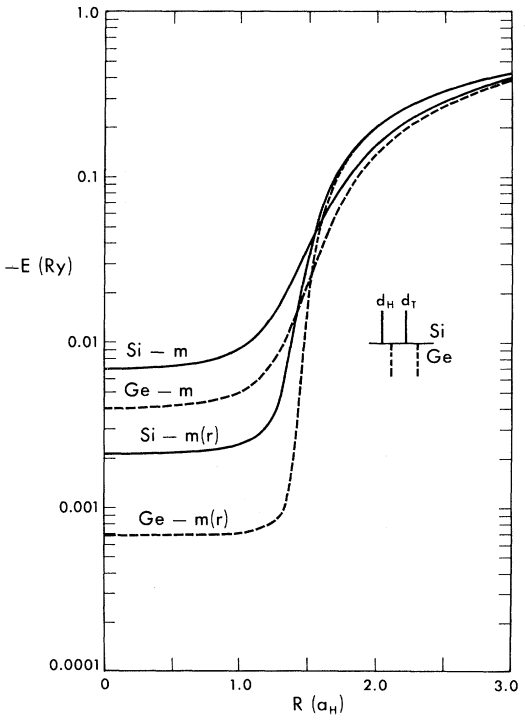

FIG. 1. Ionization energy $-E$, in units of the vacuum rydberg, as a function of the cavity radius R, units of the vacuum Bohr radius a_{H} for the cavity models. The estimated cavity radii are d_H for the hexagonal site and d_T for the tetrahedral site.

ity radius R in units of the Bohr radius in vacuum. Results are given for the potential V_C with $m(r)$ given by (3) and also for $m(r)$ equal to the constant mass m of the free electron. We used $\epsilon = 12$ and $m^* = 0.31$ for Si and $\epsilon = 15.8$ and $m^* = 0.17$ for Ge. It is seen that the transition between a shallow level (small R) and a deep level (large R) takes place quite suddenly as R is increased. There are two probable symmetrical interstitial sites for muonium in the diamond structure[12]; one with hexagonal local symmetry and one with tetrahedral local symmetry. We calculate the cavity radii d_H and d_T from the radius of the interstitial sphere that will fit inside the touching hard spheres of the lattice. In terms of the lattice parameter a we have $d_H = 0.198a$ and $d_T = 0.227a$; so that in terms of the vacuum Bohr radius a_H:

Si: $d_H = 2.03a_H$; $dT = 2.22a_H$;

Ge: $d_H = 2.12a_H$; $d_T = 2.31a_H$.

These values of the cavity radii are marked on the figures. The lattice parameters are 5.43 Å for Si and 5.66 Å for Ge. The cavity radius in ice is approximately $4a_H$. For fused quartz the cavity radius is hard to estimate.

The probability density $|\psi(0)|^2$ relative to the vacuum value is plotted in Fig. 2 as a function of the cavity radius. The results of Fig. 2 are summarized in Table I. The probability density with $m(r)$ given by (3) is higher in Si than in Ge; this order does not agree with experiment. In Fig. 2 the curves of $|\psi(0)|^2$ for Si and Ge for the mass m are close to each other. Because the cavity radius of Si is smaller than that of Ge we now obtain the right order $|\psi(0)|^2_{Ge} > |\psi(0)|^2_{Si}$, but both calculated values are high. However, the qualitative agreement with experiment of the cavity models is encouraging, and we shall discuss the mass problem[13] in more detail later. The expectation value of the muonium radius $\langle r \rangle$ in units of the vacuum Bohr radius is plotted in Fig. 3 as a function of the cavity radius. It is not surprising in view of their

TABLE I. Probability density $|\psi(0)|^2$ ratios for Si and Ge on the cavity models with the effective mass outside the cavity and with the free mass in all space. The cavity radii of the hexagonal site and of the tetrahedral site are d_H and d_T.

$m(r)$	R	$\lvert\psi(0)\rvert^2/\lvert\psi(0)\rvert^2_{vac}$ Si		Ge
$m(r) = \begin{cases} m, & r<R \\ m^*, & r>R \end{cases}$	d_H	0.578	>	0.506
	d_T	0.642	>	0.565
m	d_H	0.756	<	0.787
	d_T	0.837	<	0.860
Experimental		0.444	<	0.578

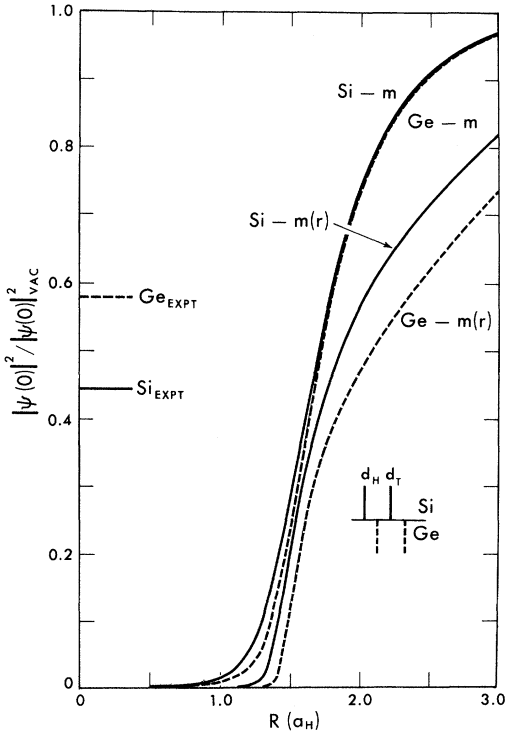

FIG. 2. Probability density ratio $|\psi(0)|^2/|\psi(0)|^2_{vac}$ for the cavity models.

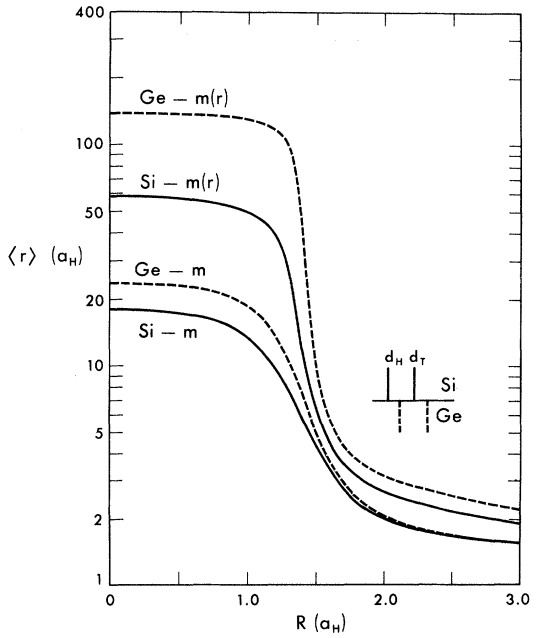

FIG. 3. Expectation value of the radius $\langle r \rangle$ for the cavity models.

TABLE II. The ionization energies $-E$, the ratios $|\psi(0)|^2/|\psi(0)|^2_{\text{vac}}$, and the expectation values of radius $\langle r\rangle$ of the solutions of the Schrödinger equations with the free-electron mass and the Coulomb potential screened by the fitted dielectric functions of Walter and Cohen and of Vinsome and Richardson.

	Si					Ge				
	Q_D (a_H^{-1})	ϵ_0	$-E$ (Ry)	$\frac{\lvert\psi(0)\rvert^2}{\lvert\psi(0)\rvert^2_{\text{vac}}}$	$\langle r\rangle$ (a_H)	Q_D (a_H^{-1})	ϵ_0	$-E$ (Ry)	$\frac{\lvert\psi(0)\rvert^2}{\lvert\psi(0)\rvert^2_{\text{vac}}}$	$\langle r\rangle$ (a_H)
Walter and Cohen	0.9153	11.47	0.112	0.427	2.617	0.8702	14.00	0.116	0.453	2.526
Vinsome and Richardson	0.9221	10.53	0.116	0.429	2.593	0.8377	14.95	0.126	0.478	2.433

large cavities that muonium in ice and fused quartz behaves much like free muonium.

DIELECTRIC FUNCTION APPROACH

A self-consistent dielectric function $\epsilon(q)$ can be calculated from the band structure.[14] Hermanson[15] has proposed the model dielectric function

$$\epsilon(q)=\epsilon_0\frac{q^2+Q_D^2}{\epsilon_0 q^2+Q_D^2}\ , \tag{4}$$

where Q_D is a fitting or screening parameter. The Fourier transform gives

$$1/\epsilon(r)=1/\epsilon_0+(1-1/\epsilon_0)\,e^{-Q_D r}\ . \tag{5}$$

The static dielectric function should be appropriate for processes at frequencies lower than the zone-average energy gap, which is about 4 eV in these crystals.

Values of $\epsilon(q)$ have been calculated also for the actual band structures of these semiconductors by Nara,[16] Walter and Cohen,[17] and Vinsome and Richardson.[18] They found only a small anisotropy in $\epsilon(q)$.

We made a least-squares fit of ϵ_0 and Q_D in (4) to the $\epsilon(q)$ of Walter and Cohen, and we then solved the Schrödinger equation with the potential $-e^2/\epsilon(r)r$, with the free-electron mass. We did another calculation with (4) fitted to the $\epsilon(q)$ of Vinsome and Richardson. The results are summarized in Table II. It is noteworthy that the Walter–Cohen dielectric function leads to probability density fractions of 0.43 for Si and 0.45 for Ge. The various dielectric functions as used are plotted in Figs. 4–6.

EFFECT OF MASS VARIATION

The electron mass to be used in the effective-mass equation is expected to be position dependent, but without the sudden discontinuity involved in the cavity assumption of (3). Hermanson has proposed an expression for $m(r)$ that is analogous to (5) for $\epsilon(r)$:

$$m/m(r)=m/m^*+(1-m/m^*)\,e^{-Q_m r}\ . \tag{6}$$

This expression has been used by Jaros[19] in the treatment of shallow donors. We have calculated

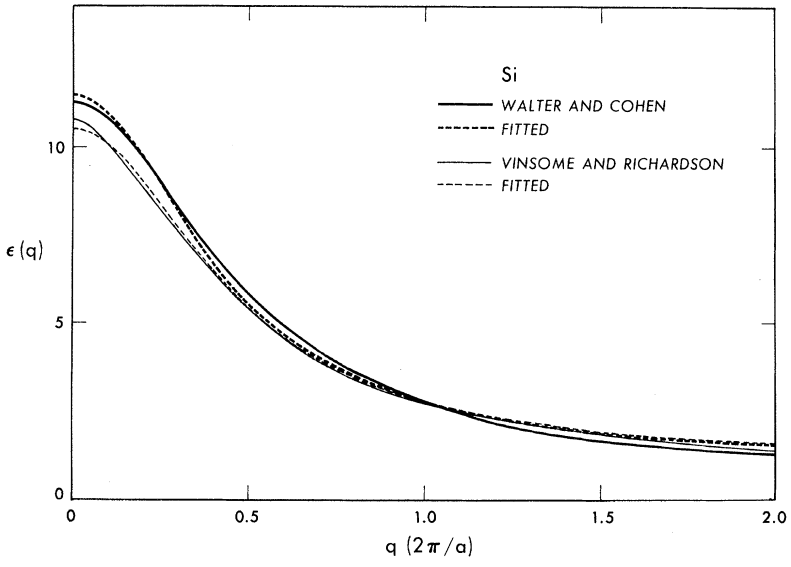

FIG. 4. $\epsilon(q)$ for Si.

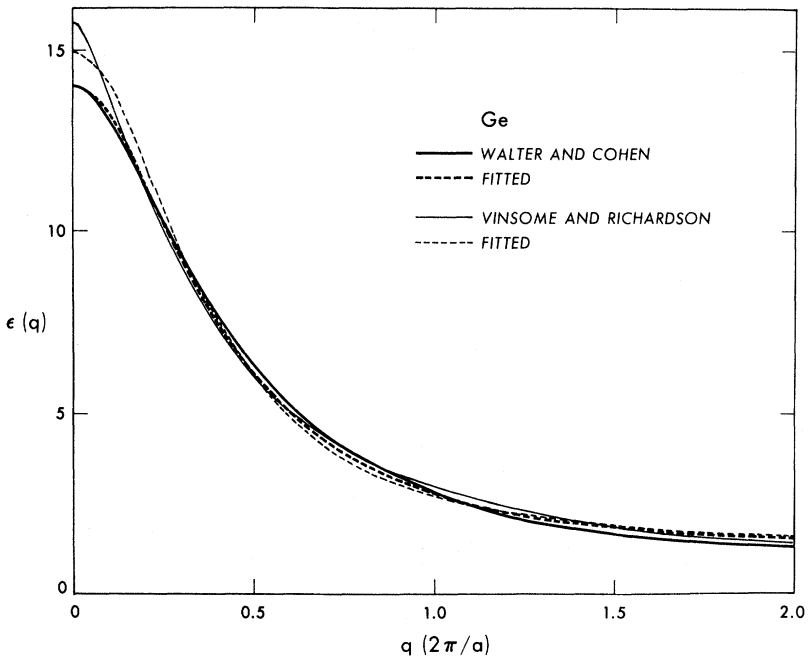

FIG. 5. $\epsilon(q)$ for Ge.

$|\psi(0)|^2$ for a variety of values of Q_m. We do not reproduce the results because it became clear that only a value of Q_m of zero or near zero (i.e., much smaller than the reciprocal nearest-neighbor distance) will give acceptable probability densities. Thus a value equal to the Q_D of the dielectric function gives values of both $|\psi(0)|^2$ and of the ionization energy that are two orders of magnitude too small! We note that for the two limiting problems with the masses m and m^* the ionization energies are not related by the Rydberg scaling $E \to (m^*/m)E$, because the potential $-e^2/\epsilon(r)r$ is not a $1/r$ potential. For a general $m(r)$ the eigenvalue problem is sensitive to the form of $m(r)$ because the operator $p^2/2m$ is replaced by the symmetrical form

$$\frac{1}{4}\left(\frac{1}{m(r)}p^2 + p^2\frac{1}{m(r)}\right).$$

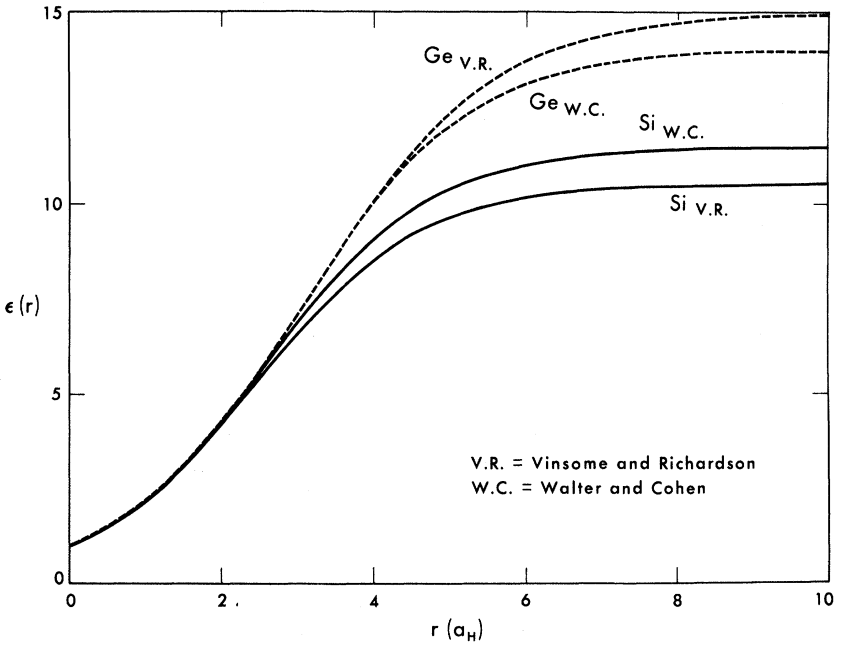

FIG. 6. $\epsilon(r)$ for Si and Ge.

DISCUSSION

To obtain an exact solution is too difficult to contemplate at present. We feel we have gone as far as we can with the means available. The observations on muonium in Si and Ge appear reasonable, theoretically. It would be enormously valuable to have ENDOR experiments on H in Si and Ge, so that one might obtain the ionization energy, identify the interstitial site, and determine the electron density on the nearby atoms of the lattice.

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[4]We are indebted to Dr. N. B. Hannay of the Bell Laboratories for a personal review of the situation, and to Professor C. D. Jeffries and Dr. J. Wolfe for communication of unpublished nonresults on a search by high-sensitivity EPR and NMR equipment. It should be noted [W. J. Choyke and L. Patrick, Phys. Rev. Lett. **29,** 355 (1972)] that ion bombardment can implant H, and in SiC a proportion of the implanted H diffuses to a vacant Si site to form a CH bond with one of the neighboring C atoms. It is possible that muons may form similar Si-μ and Ge-μ bonds, but if the center is electronically diamagnetic, it would not have a hyperfine splitting.

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Raman Scattering in α-Sn†

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The inelastic scattering of light in the presence of a magnetic field in α-Sn is discussed. Both interband and intraband Landau-level electronic transitions are considered. Calculated values of the scattering cross section and of the Raman shift for several electronic transitions indicate that observations of these scatterings should be highly feasible.

I. INTRODUCTION

Electronic Raman scattering from semiconductors has been investigated in both theory[1–5] and experiment.[6–9] These include impurity scattering and Landau-level scattering. Although most of the cases discussed involve intraband scattering, certain possible interband scatterings have been suggested. In the presence of a magnetic field, Wallis and Mills[4] suggested a process in which an interband transition to an intermediate state is followed by an intraband transition between adjacent Landau levels to the final state. In the absence of magnetic field, Burstein, Mills, and Wallis[5] discussed the possibility of a Raman scattering in which the initial, final, and intermediate states are all in different bands. Owing to selection rules, this scattering can occur only if the initial and final