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Impurity-Assisted Intervalley Electron Scattering of Germanium and Silicon under Uniaxial Compression

KAZUO MURASE and EIZO OTSUKA*

Department of Physics, Osaka University, Toyonaka, Osaka

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Application of uniaxial stress along a particular crystallographic axis of a many-valley semiconductor causes up- and down-valleys in the momentum-energy space for electrons. The cyclotron resonance linewidth of the down-valley signals are broadened as a function of stress for certain doped germanium and silicon crystals. The electron transferred from up- to down-valley has an extra kinetic energy at the down-valley, corresponding to the valley energy difference, and the observed broadening is ascribed to the raised electron temperature there. From the broadening of the down-valley signal and observed down-to-up electron population ratio, the impurity-assisted intervalley scattering frequency is estimated for Ge/Ga, Ge/In and Si/P at 4.2°K. The magnitude is 1/20~1/30 of the overall impurity scattering. There is an indication that it is strongly dependent of temperature.

§1. Introduction

Effects of uniaxial stress on the cyclotron resonance in silicon and germanium have been widely investigated both for electrons and holes. The oldest work goes back to the days of Rose-Innes,¹⁾ who demonstrated the electron repopulation between different valleys of germanium owing to the applied stress. Hensel *et al.*²⁾ used an elaborate uniaxial compression technique for the study of stress-induced variations of the band structures. Such a technique has turned out particularly useful in dealing with the valence band problems.³⁻⁵⁾ More recently, the present authors' group dealt with the stress effect on the carrier lifetime in silicon and germanium.⁶⁻⁸⁾ In this paper, a new effect of the uniaxial stress on the electron resonance linewidth is described. It is no carrier lifetime effect such as reported previously, but an entirely different phenomenon which is related to the carrier heating owing to the intervalley electron transfer. The applicability of the analysis presented here is strongly limited, yet the intervalley scattering relaxation times due to neutral group III acceptors in germanium as well as that due to phosphor in silicon are estimated. During the last decade, we have seen a number of methods to obtain the intervalley scattering rate, as such utilizing elastogalvanomagnetic effect,⁹⁾ acousto-electric effect^{10,11)} or ultrasonic attenuation.¹²⁾ These are indeed useful for the study of the intervalley scatterings

in which phonons or donor impurities are responsible, but evidently useless when dealing with acceptor-associated scatterings. In this respect, the experimental method introduced here furnishes a kind of new-type breakthrough. At first sight, one might feel the present authors to be standing on a far-fetched supposition in their interpretation of the experimental results. Related observations strongly indicate, however, that the phenomenon is due actually to the intervalley scattering. Since a little complication is involved in the way to go, we shall wander on some preparatory foregrounds before entering in proper description of our work.

§2. Theoretical Preliminaries

2a) Carrier repopulations under uniaxial stress

If one applies a uniform stress upon a many-valley semiconductor like silicon or germanium, the valley energy is shifted by the amount

$$\Delta E^{(i)} = \mathcal{E}^{(i)} : \epsilon ; \quad (1)$$

where $\mathcal{E}^{(i)}$ is a symmetric second rank tensor called the deformation potential constant and ϵ the strain caused by stress.¹³⁾ The superfix (i) stands for the *i*-th energy valley. Writing $a^{(i)}$ to denote the unit vector along the valley axis, we have

$$\mathcal{E}^{(i)} = \mathcal{E}_d \mathbf{1} + \mathcal{E}_u a^{(i)} a^{(i)}, \quad (2)$$

where the suffices *d* and *u* signify dilatation and shear, respectively.¹⁴⁾ Combining the relations (1) and (2), one finds the relative energy shift of the valleys as he applies a uniaxial stress of magnitude *X* along the vector *e* to yield

* Formal affiliation: Department of Physics, College of General Education, Osaka University.

$$\Delta E^{(i)} = \varepsilon_u X s^* \{ (a^{(i)} \cdot e)^2 - 1/3 \}; \quad (3)$$

Here

$$s^* = \frac{1}{2} s_{44} \quad \text{for Ge,}$$

and

$$= s_{11} - s_{12} \quad \text{for Si,}$$

in which s_{ij} 's are the elastic compliance constants.

For a uniaxial stress along the longest principal axis of one of the electron valleys, the valley parallel to the stress energetically goes down, while the remaining ones move up. We shall henceforth call the former "the down-valley" and the latter "up-valleys". Under the illumination of the intrinsic light, the ratio of electron populations between the down- and one of the up-valleys is given by

$$n_1/n_2 = \frac{(1+g) + \tau_{21}^0 (1+\mu)^{-1/2} / \tau_r}{(1+g) \exp(-\mu) + \tau_{21}^0 (1+\mu)^{-1/2} / \tau_r}; \quad (4)$$

where g is the multiplicity ratio of up- to down-valleys; *i.e.*, 2 for silicon and 3 for germanium, $\mu = \Delta E / k_B T$, τ_r the recombination time for electrons which we shall assume equal for up- and down-valleys, and τ_{21}^0 the intervalley scattering time constant at zero stress. The down-valley is here designated by the suffix 1 and the up-valley by 2. The factor $(1+\mu)^{-1/2}$ comes in on account of the change of the final state density in the intervalley transition. One can determine the ratio τ_{21}^0 / τ_r from (4), if he knows the variation of n_1/n_2 as a function of μ . If either τ_r or τ_{21}^0 is known, the other can readily be determined.

2b) Carrier heating due to intervalley electron transfer

It has been shown by Weinreich *et al.*¹⁰⁾ that at liquid helium temperatures contribution of phonons to intervalley scattering is negligible compared with that of impurities. In cyclotron resonance experiments, impurities are neutralized because of the intrinsic illumination. Accordingly, the main contribution to intervalley scattering comes from the neutral impurities either donors or acceptors. In Fig. 1, we show the energy dissipation processes for optically excited electrons under the application of a uniaxial stress which gives rise to the up- and down-valleys. An electron scattered elastically from up- to down-valley gains an extra kinetic energy corresponding to ΔE , the up-and-down energy difference caused by the stress. Thus the electron system in the down-valley, on the average, is warmed up if more and more electrons are

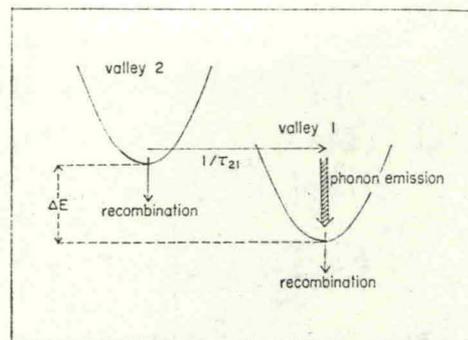


Fig. 1. Diagram showing the energy dissipation processes for the conduction electrons under the application of a uniaxial stress, which gives rise to up- and down-valleys.

poured in through this process. The elevated electron temperature would reflect itself on the resonance linewidth, provided the appropriate conditions for the carrier recombination time as well as for the intervalley transfer rate are satisfied. Assuming that the distribution function form of electrons at the down-valley does not change appreciably under stress and that the energies of the transferred electrons are not lost through electron captures by impurities, we have the relation

$$g n_2 \Delta E / \tau_{21}^0 (1+\mu)^{-1/2} = n_1 \frac{\langle \Delta \varepsilon \rangle}{2N+1} \left(\frac{1}{\tau} - \frac{1}{\tau_L} \frac{2N+1}{2N_L+1} \right), \quad (5)$$

from the energy balance requirement within the down-valley. The left-hand side gives the energy increase caused by the electron transfer from the up-valley, while the right-hand side the energy dissipation within the down-valley through electron-phonon interaction. The quantity $\langle \Delta \varepsilon \rangle$ is the mean energy lost by electron through a single collision with phonon and is given by¹⁵⁾

$$\langle \Delta \varepsilon \rangle \sim (3m^* s^2 k_B T)^{1/2}; \quad (6)$$

where s is the sound velocity, T_E the electron temperature. N is the number of phonons effective for scattering electrons at temperature T_E , N_L the number of phonons at lattice temperature T_L . In the high temperature approximation, we may put

$$N = N_L (T_L / T_E)^{1/2}. \quad (7)$$

The quantity τ is the scattering relaxation time for electrons at T_E due to acoustical phonons, which reduces to τ_L for $T_E = T_L$.

That the eq. (5) may be valid, one has to assume the following conditions:

1) Electrons elastically scattered from up-valleys promptly transfer their energies to phonons or

other electrons; or

$$(1+\mu)^{1/2}/\tau_{21}^0 < 1/\tau + 1/\tau_{e-e}. \quad (8)$$

Here $1/\tau_{e-e}$ is the electron-electron collision frequency.

2) Energy dissipation of electrons within the down-valley is dominated by electron-phonon collisions and not by captures; or

$$1/\tau_r < 1/\tau. \quad (9)$$

3) The back-flow of energy from down- to up-valley can be neglected; or

$$\exp(-\mu) < \tau_{21}^0(1+\mu)^{-1/2}/\tau_r. \quad (10)$$

This condition is satisfied only if n_1/n_2 deviates appreciably from the exponential form.

4) That the hot electrons may be supplied into the down-valley, we must have

$$\tau_{21}^0(1+\mu)^{-1/2} < \tau_r. \quad (11)$$

Combining the above condition, we find that the minimum requirement for the experimental observation of the resonance line broadening due to intervalley carrier transfer is

$$1/\tau_r < (1+\mu)^{1/2}/\tau_{21}^0 < 1/\tau. \quad (12)$$

One has further to keep it in mind that if τ_r is too long compared with τ , the relative heating-up of the down-valley electron system will not be so appreciable that an experimental observation of the line-broadening becomes difficult. There must accordingly be a point of compromise which is optimum for the experimental determination of the intervalley scattering relaxation time through the technique presented here.

2c) Carrier heating by optical excitation

In cyclotron resonance experiments, we shed the sample with the intrinsic light in order to produce the free carriers. The excess energy of an intrinsic photon over the band-gap, $h\nu - E_g$, should then convert itself into the kinetic energy of free carriers and hence one might expect a line-broadening due to the hot electron effect. In ordinary cyclotron resonance of pure materials, however, one can scarcely observe a line-broadening of this cause. It is believed that this is because of the carrier recombination time which is quite long compared with the thermalization time. Under such a condition nearly the whole carrier population must be in thermal equilibrium and any heating due to photo-excited carriers is practically unobservable. If the carrier recombination time becomes sufficiently short, one might expect a possibility of observing optical hot electrons. However, our cyclotron resonance studies of doped silicon and germanium with short

carrier lifetimes so far have never detected the presence of optical hot electrons.^{7,8,16)} In a later section, we shall see a further evidence that carrier heating of this cause is not playing any role in the present experiment.

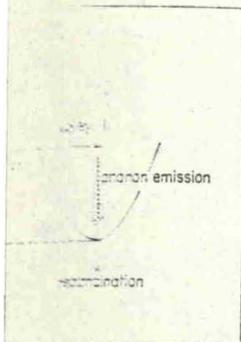
§3. Experimental Procedures

Various samples have been taken for measurement; germanium: pure, doped with indium, gallium, antimony or tin; silicon: doped with phosphor, lithium or boron. Samples employed in the experiment are listed up in Table I. The

Table I. List of the samples taken for measurement.

Sample	Impurity concentration (cm ⁻³)
Pure Ge	—
Ge/In-3	1.4×10^{15}
Ge/In-4	6.8×10^{15}
Ge/Ga-1	$3.5_5 \times 10^{14}$
Ge/Ga-2	$1.1_5 \times 10^{15}$
Ge/Sn	$\sim 10^{17}$
Si/P	8.8×10^{13}
Si/Li	5.9×10^{13}
Si/B	4.3×10^{14}

analysis described in 2b) has not always been successful because of the failure of the conditions (12) or too long a recombination time. All of the doped samples have been cut out of the same blocks used previously for the study of intravalley electron scattering due to neutralized impurities.^{8,16)} The common sample shape is a rectangular parallelepiped having the dimension of $1 \times 1 \times 3$ mm³, with its long axis along $\langle 111 \rangle$ for germanium and $\langle 100 \rangle$ for silicon. The uniaxial stress is applied along the long axis of each sample through the technique described elsewhere.¹⁷⁾ The magnetic field is rotated in the (111) plane for germanium and (100) for silicon; *i.e.*, in the planes perpendicular to the stress direction. The linewidth measurement has been carried out at the geometry, where the resolution of resonance lines is good enough. In all cases, the major axis of the down-valley ellipsoid is perpendicular to the magnetic field and the corresponding linewidth is given in terms of the relaxation time as $1/2(1/\tau_{\parallel} + 1/\tau_{\perp})$ in the Herring-Vogt notations.¹⁴⁾ All of the remaining valleys are "up-valleys." The microwave system employed is a 35.3 GHz nonresonant superheterodyne spectrometer with



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$$\frac{1}{\tau_L} \frac{2N-1}{2N_2-1}, \quad (5)$$

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$$(k_B T)^{-1/2}; \quad (6)$$

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a horizontal E -bent mitred corner close to the sample position. The microwave electric field is parallel to the stress direction and always perpendicular to the magnetic field.¹⁷⁾ Since the cyclotron resonance absorption intensity is inversely proportional to the effective mass along the microwave electric field, one has to be careful when he measures the population ratio n_1/n_2 through the peak heights. For germanium, the relevant effective mass m_B^* for the down-valley is nearly fifteen times as large as those for the up-valleys, which are all the same for the present geometry. For silicon, the corresponding mass ratio is close to five. These factors ought to be multiplied to the apparent intensity of the down-valley signal in order to get the relative electron population.

Because of the reasons stated in 2c), it is helpful to see some spectral photoresponse of the samples for the excitation light. Use is made of the white light, lights after water filters having various thickness for germanium and similar filters with aqueous solution of CuCl_2 for silicon. Properties of those liquid filters are given in the articles by Collins¹⁸⁾ and Haynes.¹⁹⁾ They are effective for cutting the extrinsic light off, while passing almost the whole intrinsic part above the band-gap threshold.

§4. Results

Before describing the experimental results, we shall mention, for some length, the cyclotron resonance signal response through optical filters. In the case of pure materials, use of any filter merely reduced the signal intensity by the degree which depends on the thickness or bandwidth of the filter. The linewidth of the resonance signal, on the other hand, always remained the same. The irrelevance of the linewidth to the effective photon energies is not surprising, since the electron thermalization occurs much faster than recombination. In that case, the high energy photons are contributing to the cyclotron resonance signal without raising the electron temperature. One might then expect the optical hot electron effect, when he deals with doped materials whose carrier lifetime is sufficiently short. The main materials in the present work are Ge/In and Ge/Ga. To the authors' surprise, it is found that contribution of high energy photons to the cyclotron resonance signals are completely absent for these materials. Namely, insertion of a water filter, the thickness of which is less than 1 mm, reduced the signal intensity to null. This poses a striking contrast

to the case of pure germanium, in which the signal intensity through a 10 mm thick water filter remained not less than a tenth of that under the white light illumination. Quite a similar situation prevails in the case of doped silicon, the corresponding filter being an aqueous solution of CuCl_2 . We shall not be engaged here in the actual elementary process itself, but suffice it to say that a series of filter experiment has added a further evidence that high energy photons are not contributing to the cyclotron resonance signal in doped materials. In fact, this has been an implicit basis for the successful analyses of our previous works.^{7,8,16)} Hence we shall forget all about the optical hot electrons. If we observe any hot electron effect, therefore, that is considered due solely to intervalley transfer.

Figure 2.a) shows the variation of linewidth of

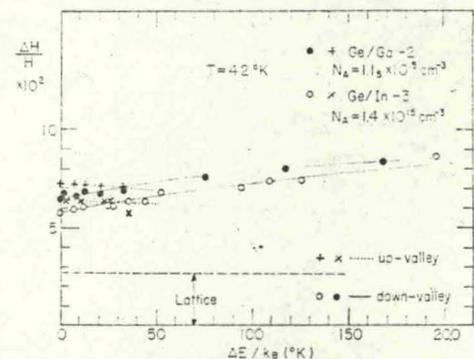


Fig. 2. a) Variations of cyclotron resonance linewidths against stress for two typical p -type germanium crystals at 4.2°K . Only the down-valley signals are broadened. Contribution from the lattice scattering at $T_B = T_L$ is shown by a broken line.

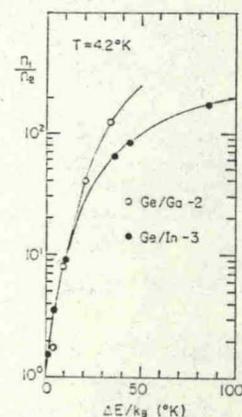
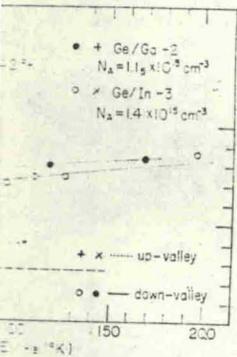


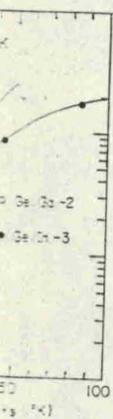
Fig. 2. b) Down-to-up valley population ratios for the same crystals as shown in a) against stress at 4.2°K .

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the down-valley electron signals against up-and-down energy difference, which is expressed in terms of temperature,* for two samples measured at 4.2°K. One may note that the relative linewidth $\Delta H/H$ increases on application of stress. In the same figure is also shown the linewidth variation of one of the up-valley signals. Because of the rapid sinking-down of the up-valley signals with increasing stress, one is unable to trace the linewidth beyond a certain stage of stress, but it appears to have a slight decreasing tendency at the beginning. The microwave power is so tuned at zero stress as to give a sufficiently good unheated electron signal for the down-valley. The down-valley system, accordingly, is initially unheated, while the up-valley system is likely heated at zero stress because of the smaller m_{eff} . The subsequent changes of linewidths on application of stress are connected with the intervalley electron transfer. The broadening of the down-valley signal is considered due to the hot electrons which came from the up-valleys, while the narrowing of the up-valley signal would be due to the cooling of the valley owing to the escape of high energy electrons to the down-valley.

Figure 2.b) shows the variation of the population ratio n_1/n_2 against $\Delta E/k_B$. From this combined with the observed down-valley broadening as shown in Fig. 2 and the energy balance equation (5), one is able to calculate $1/\tau_{21}^0$, or the intervalley scattering frequency. Values successfully obtained at 4.2°K are listed in Table II for typical speci-

Table II. Impurity-assisted intervalley scattering frequency at 4.2°K for typical doped samples. The overall impurity scattering frequencies ($1/\tau_I$'s) are also shown for comparison.^{8,16)}

Sample	$1/\tau_{21}^0$ (sec ⁻¹)	$1/\tau_I$ (sec ⁻¹)
Ge/Ga-1	$(6 \pm 1) \times 10^7$	1.2×10^8
Ge/Ga-2	$(1.5 \pm 0.3) \times 10^8$	4.1×10^8
Ge/In-3	$(1.1 \pm 0.3) \times 10^8$	2.9×10^8
Si/P	$(1.4 \pm 0.2) \times 10^8$	2.7×10^8

mens. The calculations have been carried out at a stress corresponding to $\Delta E/k_B = 40^\circ\text{K}$, where the conditions (12) are satisfied. The table includes the results for Ge/Ga-1 and Si/P, which are not shown in Fig. 2. For comparison, the overall (both intra- and intervalley) impurity scattering

* The value of ϵ_u used here is 19.3 eV, which is determined from the initial slope of the In (n_1/n_2) vs. stress curve for various samples.²⁰⁾

frequency $1/\tau_I$ is listed for each sample.^{8,16)} One can see that $1/\tau_{21}^0$ is nearly proportional to impurity concentration for Ge/Ga.

From the value of τ_{21}^0 thus derived and the relation (4) for n_1/n_2 combined with the observation shown in Fig. 5, one can also obtain information about the recombination time, say $1/\tau_r = 4.4 \times 10^7 \text{ sec}^{-1}$ for Ge/In-3 and $1.2 \times 10^7 \text{ sec}^{-1}$ for Ge/Ga-2 at $\Delta E/k_B = 40^\circ\text{K}$. That is to say, the conditions (12) are satisfied for these materials at 4.2°K.

Attempts were made to extend the measurement below 4.2°K. The low temperature stress measurement has been difficult on account of the shorter carrier lifetime and, in some cases, the appearance of a large background photoconductive signal.¹⁶⁾ The requirements (12) also tend to break down, since τ_r is found strongly temperature dependent. Relatively satisfactory results for Ge/In-3 at 3.2°K are given in Fig. 3.a) and b). The rise of the linewidth for the down-valley signal on application of stress is steeper than that

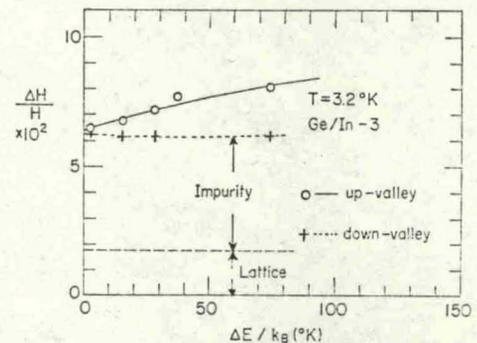


Fig. 3. a) Variation of linewidths for Ge/In-3 at 3.2°K. Broadening of the down-valley signal is enhanced compared with that at 4.2°K, while the width of the up-valley signal practically remains constant.

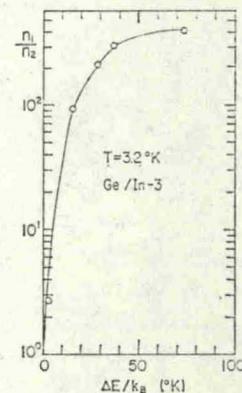


Fig. 3. b) The corresponding variation of the population ratio.

at 4.2°K. The linewidth of the up-valley signal, on the other hand, remains unchanged. That is, possibly because of the shorter carrier lifetime at 3.2°K, than at 4.2°K, rise of the up-valley electron temperature is negligible even for zero stress. The intervalley transfer frequency $1/\tau_{21}^0$ derived at $\Delta E/k_B=40^\circ\text{K}$ is $6 \times 10^8 \text{ sec}^{-1}$, or more than five times as large as that at 4.2°K.

Finally, we shall briefly mention the results for Ge/In-4 and Ge/Sn. Figure 4.a) gives the observed

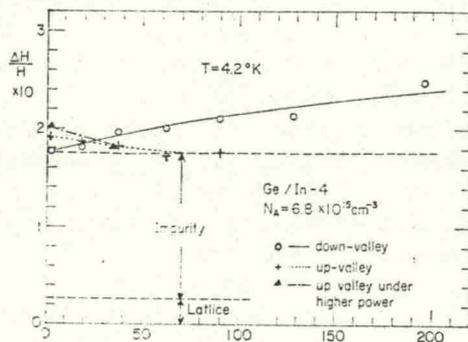


Fig. 4. a) Variation of linewidths for Ge/In-4 at 4.2°K. Initial narrowing of the up-valley signal is more pronounced for an increased microwave power.

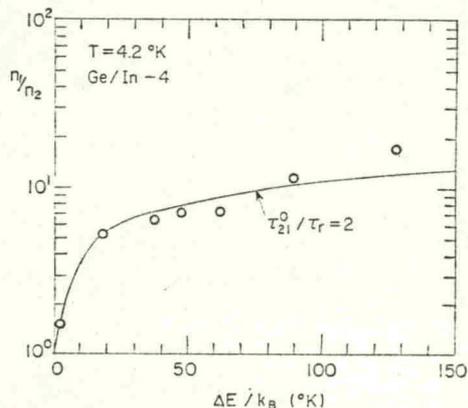


Fig. 4. b) The population ratio is fitted by a theoretical curve with the adjustable parameter $\tau_{21}^0/\tau_r=2$.

broadening of Ge/In-4 at 4.2°K and Fig. 4.b) the corresponding population ratio. Though the broadening is observed, $1/\tau_{21}^0$ calculated at $\Delta E/k_B=40^\circ\text{K}$ is only one-third of that expected from the result for Ge/In-3. Probably one may account for this by too short a relaxation time; if we assume $1/\tau_{21}^0$ to be proportional to impurity concentration, we have $1/\tau_r=1.1 \times 10^9 \text{ sec}^{-1}$ for Ge/In-4 at $\Delta E/k_B=40^\circ\text{K}$. Since $1/\tau \sim 1/\tau_L=4.2 \times 10^9 \text{ sec}^{-1}$,¹⁶⁾ the conditions (12) would not be satisfied too well. Here one may note that comparison with the result for Ge/In-3 stated above

indicates a relation of the type $1/\tau_r \propto N_{\text{In}}^2$, where N_{In} is the concentration of indium. Of course it is still too premature to draw any definite conclusion about the concentration dependence of $1/\tau_r$, but one finds that at least τ_{21}^0 and τ_r are in no way proportional to each other; otherwise we should always have the same n_1/n_2 vs. $\Delta E/k_B$ curve for any material and at any temperature. For Ge/Sn, no down-valley broadening is observed at 4.2°K; but at 1.5°K, a very slight broadening is visible. The dopant tin, being an isoelectronic with germanium, does not make the carrier lifetime so short that behaviors at 4.2°K are rather like those of pure germanium. Nevertheless, the carrier lifetime seems to decrease as one goes to lower temperatures and the condition for observability of the broadening is more favored at 1.5°K. It is not certain, however the broadening at 1.5°K is caused by tin or by other residual impurities. Hence no quantitative analysis has been carried out.

§ 5. Discussions

The analysis presented here is based on the assumption that optical hot electrons are completely out of stage. This is not a new assumption, but has always been taken for granted in dealing with the cyclotron resonance of doped materials with short carrier lifetime.^{7,8,13)} In fact, the nice proportionality of the scattering relaxation time as well as carrier lifetime, which are derived from the extra linewidth of the resonance signal, to the dopant concentration cannot be explained without the above assumption. The completely different behaviors of up- and down-valleys also strongly refute the possible existence of optical hot electrons. Moreover, the filter experience furnishes another new experimental evidence of the ineffectiveness of the high energy photons. The perfect disappearance of the cyclotron resonance signal on insertion of a very thin water filter is even dramatic and one is naturally inclined to ask the reason. Perhaps this phenomenon is connected with an impurity-sensitive surface recombination of the optically produced free carries. The elementary process of the surface recombination at a doped germanium (or silicon) itself would certainly make an interesting physics, but the present experimental data do not offer enough materials for further discussions.*

* The ineffectiveness of high energy photons in the white light illumination for producing photocarriers is also observed by A. Honig's group for doped silicon (private communication).

of the type $1/\tau_r \propto N_{In}^2$, where N_{In} is the concentration of indium. Of course it is not possible to draw any definite concentration dependence of τ_r at least τ_{21}^0 and τ_r are in no way related to each other; otherwise we would expect the same n_1/n_2 vs. $\Delta E/k_B$ behavior in germanium and at any temperature. Intervalley broadening is observed in germanium at 4.2°K, a very slight broadening is observed in silicon, being an isoelectronic impurity. These results do not make the carrier life-time behaviors at 4.2°K are rather different in germanium. Nevertheless, the carrier lifetime is expected to decrease as one goes to higher temperatures and the condition for observing intervalley scattering is more favored at 1.5°K. However, the broadening at 1.5°K is not due to other residual impurities. This analysis has been carried

out. The analysis presented here is based on the assumption that the optical hot electrons are completely thermalized. This is not a new assumption. It has been taken for granted in the analysis of cyclotron resonance of doped semiconductors. In fact, the carrier lifetime, which are independent of the resonance frequency, cannot be explained by the above assumption. The different behaviors of up- and down-valley signals do not refute the possible existence of intervalley scattering. Moreover, the filter method is another new experimental method. The effectiveness of the high energy filter method for the disappearance of the cyclotron resonance on insertion of a very thin layer of impurity is dramatic and one is naturally inclined to believe this. Perhaps this method is well suited with an impurity-sensitive impurity. The observation of the optically produced carrier lifetime is an elementary process of the carrier lifetime in a doped germanium (or silicon). These results certainly make an interesting contribution. The present experimental data do not preclude further discussions.*

The observation of high energy photons in the process of producing photoconductivity by A. Honig's group for further communication).

Whereas the optical hot carriers are killed at the surface, the hot electrons due to intervalley transfer remain alive all over the bulk part of the sample, and hence contribute to the cyclotron resonance signal.

One might argue that the observed broadening of the down-valley signal is not necessarily associated with the intervalley electron transfer, but possibly with the change of the acceptor wave function. This idea faces a difficulty, however, when one recalls that only the down-valley signal is broadened. The up-valley signal should certainly be affected similarly, if the broadening is due to the change of the acceptor wave function. What we have observed, however, is that the up-valley signal remains of the same linewidth if it is not initially heated and is even narrowed if it is slightly heated at zero stress. If our interpretation of the stress-broadening of the down-valley signal is correct, the latter effect, or narrowing of the up-valley signal, no doubt is "cooling" due to the escape of high-energy electrons. This is analogous to the evaporation cooling of a liquid.

The value of τ_{21}^0 derived here is for $\Delta E/k_B = 40^\circ\text{K}$, in other words, under a finite stress application. There is no guarantee that τ_{21}^0 is stress-independent. The stress-dependence mentioned here is not due to the factor $(1+\mu)^{-1/2}$ which enters because of the state density consideration, but due possibly to the change of the acceptor state. A close intercomparison of Fig. 3 and Fig. 4 leads to an indication that τ_{21}^0 has a slight decreasing tendency as one reduces the stress. Though the accurate determination of τ_{21}^0 at low stress becomes difficult, one might have to expect a variation by a factor of not more than three.

A fundamental difference of the present work from those reported previously⁹⁻¹² is that here we can deal with electron intervalley scattering even in *p*-type materials. But the condition for observability is rather critical and the method cannot always be successful. For example, one cannot extend the measurement at will for a wide range of impurity concentration or temperature. Even for a similarly doped *p*-type material, the method completely fails to apply if it is silicon. The difference is that in germanium electron is first captured by neutral acceptor very softly and then reemitted into a different valley, while in silicon the electron capture by neutral acceptor leads to on-the-spot electron-hole recombination⁹

because of the stronger binding energy of the "positronium." In the latter case we have seen that $1/\tau_r$ is quite proportional to the acceptor concentration. The electron capture probability by a neutral group III acceptor in silicon is also much larger than that in germanium and the electron resonance line is already broadened by the lifetime effect. In such a case, however, one may seek an alternative way of finding the intervalley scattering frequency; namely, one can determine the carrier recombination time through the procedure described in ref. 8) and then in turn obtain the desired intervalley scattering time from eq. (5). In fact, this type of analysis has been carried out for Si/B, and an intervalley scattering rate smaller by an order of magnitude than the recombination rate is obtained at 2.2°K*.

In conclusion, we may say that the present method can provide complementary data to those by Weinreich *et al.*^{10,11} as well as to those by other methods.^{9,12} It has a merit of being able to deal with *p*-type materials and this largely compensates the limited applicability of the method. In the case of extremely short carrier recombination time, an alternative method becomes available. Thus the stress-associated cyclotron resonance technique as a whole finds many ways of use in getting informations of impurity-assisted intervalley scattering for silicon and germanium at liquid helium temperatures.

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* Details are to be presented in a future paper together with related phenomena.

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Critical Anomaly of Sound Attenuation and Thermal Conduction in KH_2PO_4 -Type Ferroelectric Crystals^{*}

Masayoshi INOUE

Department of Physics, Faculty of Science, Kyushu University, Fukuoka

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The sound attenuation α_k and the thermal conductivity λ in the KH_2PO_4 -type ferroelectric crystals near the critical point are studied, employing the soft-mode model proposed by Kobayashi and then introducing an interaction between the acoustical phonons and the ferroelectric optical phonons. It is thus shown that λ has a dip, as observed, and α_k has a peak at the Curie point, resulting from the critical decrease in the frequency of ferroelectric mode. Thus it turns out that the acoustical phonon couples strongly with the ferroelectric mode of the $[\text{K-PO}_4]$ lattice vibration through the third-order anharmonic interaction.

§ 1. Introduction

The dynamical aspects of the second-order phase transitions have been recently studied both experimentally and theoretically. Relaxation and transport phenomena show anomalies when the temperature approaches the critical point. For instance, anomalies in the thermal conductivity¹⁾ and the sound attenuation²⁾ have been observed in certain magnetic crystals. Experiments on ferroelectric crystals^{3,4)} reveal that the thermal conductivity has an anomalous dip near the Curie temperature which has been treated theoretically by the present author in the case of BaTiO_3 .⁵⁾

Ultrasonic attenuation measurements also show

that the attenuation constants of ferroelectric crystals have peaks in the neighbourhood of their transition points.⁶⁾ Since Landau-Khalatnikov's⁷⁾ phenomenological theory, these anomalous behaviours have been much investigated, especially in the case of displacive-type ferroelectrics such as BaTiO_3 . Recently Tani and Tsuda⁸⁾ also have calculated the attenuation constant with the use of Silverman's model.⁹⁾

In the present paper, we shall study the critical anomaly in the sound attenuation and thermal conductivity in the KH_2PO_4 -type ferroelectrics, introducing the interaction between the acoustic phonons and the ferroelectric optical phonons and taking into account the damping effect of the random force.

Our preliminary report, where the damping

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