Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials Sciences Division

Presented at the Twenty-Second International Conference
on the Physics of Semiconductors, Vancouver, B.C., Canada,
August 14-19, 1994, and to be published in the Proceedings

Physics with Isotopically Controlled Semiconductors

E.E. Haller

August 1994

RECEIVED
OCT 07 1994
OSTI

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PHYSICS WITH ISOTOPICALLY CONTROLLED SEMICONDUCTORS

E.E. HALLER

Materials Science and Mineral Engineering Dept.
University of California

and

MATERIALS SCIENCES DIVISION and ENGINEERING DIVISION
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Proc. 22nd International Conference on the Physics of Semiconductors,
Vancouver, B.C., Canada, August 14-19, 1994

AUGUST 1994

This work was supported in part by The Lawrence Berkeley Laboratory Directed Research and Development Program through US DOE Contract DE-AC03-76SF00098, and in part by the US National Science Foundation Center for Particle Astrophysics contract ADT-8809616.

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

87D

PHYSICS WITH ISOTOPICALLY CONTROLLED SEMICONDUCTORS

E. E. HALLER

Lawrence Berkeley Laboratory and
University of California, Berkeley CA 94720 USA

ABSTRACT

Control of the isotopic composition of semiconductors offers a wide range of new scientific opportunities. In this paper a number of recent results obtained with isotopically pure as well as deliberately mixed diamond and Ge bulk single crystals and Ge isotope superlattices will be reviewed. Isotopic composition affects several properties such as phonon energies, bandstructure and lattice constant in subtle but theoretically well understood ways. Large effects are observed for thermal conductivity, local vibrational modes of impurities and after neutron transmutation doping (NTD). Several experiments which could profit greatly from isotope control are proposed.

1. Introduction

All elemental and most compound semiconductors and their alloys contain elements which consist of more than one stable isotope. The most commonly used semiconductor silicon is composed of the three isotopes $^{28}_{14}\text{Si}$, $^{29}_{14}\text{Si}$ and $^{30}_{14}\text{Si}$ with abundances of 92.23%, 4.67% and 3.10%, respectively. The important compound semiconductor GaAs consists of mono-isotopic $^{75}_{33}\text{As}$ and the two Ga isotopes $^{69}_{31}\text{Ga}$ and $^{71}_{31}\text{Ga}$ at abundances of approximately 60% and 40%, respectively. These abundances are a consequence of the nucleosynthesis processes which led to the formation of the elements making up the matter in our region of the universe.

Most physical properties of semiconductor crystals depend to some degree on their isotopic composition. Though these dependencies are rather weak for many properties, they nevertheless teach us a lot about the origin of some basic physical processes occurring in a crystal and our level of theoretical understanding.

Not all isotope effects are subtle, however. Geballe and Hull¹ demonstrated experimentally the increase in low temperature thermal conductivity in Ge which was predicted by Pomeranchuk as early as 1942.² The room temperature thermal conductivity of isotopically controlled diamond, for example, has been shown to change by tens of percent depending on the isotopic composition. By far the largest effects due to isotopic composition can occur after the capture of a thermal neutron by the nucleus of a specific isotope. The new nucleus is either stable and the element remains unchanged or it decays forming a different element. In recent years the NTD process has been extensively applied to ultra-pure Ge used in the fabrication of very low temperature thermistors operating in the few degrees Kelvin down to the milliK range.³ Isotope superlattices of $^{69}_{31}\text{GaAs}$ and $^{71}_{31}\text{GaAs}$ have been grown for the study of Ga self-diffusion⁴ in GaAs. Using the NTD technique, isotope superlattices can be selectively doped after

they have been grown.⁵ The doping level may be increased in finished devices by re-immersion of the crystal in a thermal neutron bath.

2. Materials Aspects

Focusing on those elements which are of importance for semiconductors either by being a constituent of the semiconductor lattice or by acting as a neutral, shallow- or deep-level impurity, we find that nature provides an interesting and useful mixture of mono- and poly-isotopic elements.

Even under very favorable circumstances isotope separation will remain costly and ways have to be found to minimize materials use. This limitation naturally favors thin films which can be grown on inexpensive substrates of natural composition. It appears fortuitous that a majority of current scientific studies and of electronic and optoelectronic devices make use of thin film structures. It may be necessary to develop special low volume sources for MBE systems and to optimize the use of feed gases for chemical vapor deposition (CVD) related growth processes.

For bulk crystal studies one has to resort to the growth of small crystals. Both the purity and the crystallographic quality (dislocation density, stacking faults) are not easily controlled as one moves to very small crystals. Again, using enriched Ge isotopes we have succeeded in growing randomly seeded single crystals with volumes of the order of $1\text{-}2\text{ cm}^{-3}$ and net-dopant concentrations $\leq 10^{12}\text{ cm}^{-3}$.⁶ A split graphite crucible in a vertical freeze configuration was used for this purpose.

The growth of isotopically controlled diamond strongly differs from the standard semiconductor crystal growth techniques and has been described by Banholzer and Anthony.⁷

3. Phonons and Related Properties

The dependence of the phonon frequency ω on mass M can be described in the Virtual Crystal Approximation (VCA) by

$$\omega \propto M^{-1/2}. \quad (1)$$

Raman Spectroscopy and Photoluminescence (PL) have been used for the study of isotopically enriched and deliberately mixed germanium crystals. The Raman studies were mostly performed by the members of the group of M. Cardona.⁸ What is surprising at first sight is the very weak dependence of the phonon line width of $\sim 1\text{ cm}^{-1}$ on isotopic composition. The explanation is found in the ion mass fluctuation bandwidth of Ge which is much smaller than the intrinsic optical phonon bandwidth. Under these circumstances phonons do not become localized but remain spread out over a large number of unit cells, leading to a close to perfect linear averaging of the various isotope masses. The linewidth has been shown to be due to the phonon lifetime for the anharmonic decay into two phonons.

Photoluminescence studies of several isotopically enriched Ge crystals were first reported by Davies *et al.*^{9,10} Fig. 1 shows representative luminescence spectra of highly enriched ^{70}Ge and ^{74}Ge crystals. The LA and the TO phonon assisted free exciton (FE) lines are clearly shifted in energy. Excitons bound to deliberately introduced substitutional Cu acceptors and P donors generate both phonon assisted (TA, LA, TO) as well as no-phonon lines (np). Whereas the phonon assisted lines suffer shifts due to phonon and bandgap energy changes, the np lines are displaced solely

Figure 1. Luminescence from the decay of free excitons and excitons bound to Cu acceptors and P donors in ^{70}Ge and ^{74}Ge at 4.2K. (Courtesy of Gordon Davies *et al.*).⁹

Figure 2. Thermal conductivity of natural abundance (1.1% ^{13}C) diamond (lower squares), isotopically enriched (0.1% ^{13}C) diamond (upper squares), together with low temperature data (circles) and high temperature data (crosses). The solid curves are the result of a theoretical fit to the data, using the same set of fitting parameters. The inset shows the calculated thermal conductivity corresponding to 1%, 0.1%, and 0.001% ^{13}C concentrations. (Adapted from Lanhua Wei *et al.*).¹³

because of bandgap changes. This rich information allows the quantitative determination of isotope-related phonon and bandgap changes.

Stimulated in part by speculations regarding very large increases of the thermal conductivity in **isotopically pure diamonds**, a series of diamond crystal growth and characterization studies with extensive theoretical interpretation has been conducted. The thermal conductivity of dielectrics is given by

$$K = \frac{1}{3} C v L, \quad (2)$$

with C = specific heat, v = phonon velocity and L = phonon mean-free path. Neither the velocity of low-frequency phonons nor the specific heat are predicted to change much at a 1.1% ^{13}C isotope impurity level in natural diamond. The large thermal conductivity increase which is observed for diamonds with increasing isotopic purity (Fig. 2) must therefore be due to changes in the **phonon scattering rates**.

Lattice parameter determinations have been conducted for several isotopically mixed diamonds. Fig. 3 shows the experimental data obtained by Holloway *et al.*¹¹ The data can be fitted to:

$$a_0(T = 25^\circ\text{C}, x) = [3.56714 - 0.00054x] (\text{\AA}) \quad (3)$$

In an elegant experiment Ramdas *et al.*¹² have determined the elastic moduli of highly enriched ^{13}C diamond using Brillouin shifts in inelastically scattered monochromatic radiation from LA phonons traveling along the $\langle 100 \rangle$ and the $\langle 111 \rangle$ crystal orientations. These measurements show that the elastic moduli are 0.5% higher for ^{13}C diamonds as compared to natural diamonds. Using an empirical relationship between hardness H and the elastic modulus c_{11} ($c_{11} \propto H^{7/4}$), Ramdas *et al.*¹² supported their claim that ^{13}C diamonds are the **hardest terrestrial material** and represent the solid with the highest atom density.

The isotopic composition affects the **bandstructure** through the electron-phonon coupling and through the change of the crystal volume with isotopic mass. Several groups have conducted low temperature studies of the direct and indirect bandgaps of

natural and isotopically controlled Ge single crystals.^{9, 14, 15} Measurement of the energies of impurity-bound excitons shown in Fig. 1 permits the direct determination of bandgap shifts with the crystal isotope mass because the radiative recombination does not require phonon participation. The rate of bandgap energy change which is equal to the exciton binding energy change with isotope mass as determined by Davies *et al.*⁹ is

$$dE_{IG}/dA = dE_{NP}/dA = 0.35 \pm 0.02 \text{ meV/amu} . \quad (4)$$

Figure 3. Isotopic dependence of the lattice constant of diamond at 25°C. The line is a least square fit to the data (Courtesy of A. Holloway *et al.*).¹¹

The contribution to the bandgap shift originating in the volume change can be estimated using the lattice constant change with isotope mass and the dependence of E_{IG} with volume:

$$(dE_{IG}/dA)_{vol} = 0.132 \text{ meV/amu} \quad (5)$$

The main contribution to dE/dA can be directly related to the change of the energy gap with temperature. This change is described by structure factors which contain electron-phonon interaction terms (Debye-Waller factors) and self-energy terms. For practical calculations these terms are expanded in a power series of the atomic displacements. The leading terms are proportional to the mean-square displacements $\langle u^2 \rangle$ of each atom. Describing the lattice atoms in terms of harmonic oscillators one finds:

$$\langle u^2 \rangle = \hbar \left(\frac{1}{2} + n \right) / M \omega . \quad (6)$$

With increasing temperature both n and $\langle u^2 \rangle$ increase leading to the observed reduction of the energy gap. At low temperature $n = 0$ and we only deal with the zero-point oscillation. Combining the dependence of ω on M with the above equation we find:

$$\langle u^2 \rangle \propto 1/\sqrt{M} . \quad (7)$$

Zollner *et al.*¹⁶ have performed a numerical calculation of the isotope dependence of the electronic bands using an empirical pseudopotential method including the necessary lattice dynamics. They find for Ge $(dE_{IG}/dA)_{e-p} = 0.41 \text{ meV}$. The total calculated shift of the indirect bandgap energy with isotope mass adds up to $(dE_{IG}/dA)_{total} = 0.48 \text{ meV}$. This result compares favorably with the experimental values stated above.

Measurements of the **direct bandgap** at the Γ point ($\vec{k} = 0$) in the Brillouin zone have also been performed by Davies *et al.*¹⁰ who used low temperature optical absorption measurements of very thin samples of Ge single crystals with natural composition and of three different, highly enriched isotopes. They found

$$dE/dA = 0.49 \pm 0.03 \text{ meV/amu} \quad (8)$$

for the temperature extrapolated to zero. Parks *et al.*¹⁷ have used piezo- and photo-modulated reflectivity spectra of four monoisotopic and one natural Ge crystals.

The growth and study of **isotope superlattices** was proposed by this author in the context of selective doping with the NTD technique.⁵ The vibrational modes for a $^{70}\text{Ge}_4/^{76}\text{Ge}_4$ [001] superlattice at $\vec{k} = 0$ were calculated using the planar force constant

model.¹⁸ Zone folding leads to states at $\vec{k}=0$ which do not exist in the bulk material. The highest energy state exhibits very little dispersion and corresponds to phonons which are strongly localized in the ^{70}Ge layers. Using the bond polarizability model¹⁹ the Raman spectrum of the two highest states have been calculated. These theoretical predictions were recently tested with Raman studies of a series of MBE grown short period isotope superlattices of ^{70}Ge and ^{74}Ge .²⁰ The shortest periods studied consisted of two atomic layers each and produce a single Raman line corresponding to the LO phonon in a crystal with isotope mass $A = 72$, the linear average of the two masses. In the $n=12$ superlattice we observe at least three strong Raman lines. For $n=32$ the Raman spectra begin to approach the structure we would expect to observe for isotopically pure bulk crystals, one made up of ^{70}Ge , the other of ^{74}Ge . Localization of the different phonon modes in each layer is practically complete at this point.

4. Local Vibrational Mode Spectroscopy

Local vibrational mode (LVM) spectroscopy is a well established research tool for the study of impurities and impurity complexes in semiconductors. In order to give an illustration of the effect of isotope enrichment on spectral complexity we want to briefly review the results on bond centered O in natural and isotopically controlled Ge. The $^x\text{Ge-O-}^y\text{Ge}$ molecule has three fundamental modes. The "wag" mode (v_3) has the

Figure 4. (a) Spectrum of the Ge_2O quasi molecules in natural Ge at 2.05 K. Eleven lines split by v_2+v_3 coupling excitations correspond to the distinct isotopic mass combinations of the two Ge atoms in the quasi molecule. An oxygen free sample produced the dashed line. The lines labeled ^{75}Ge and ^{71}Ge are caused by traces of ^{74}Ge in ^{76}Ge and ^{72}Ge in ^{70}Ge , respectively; (b) spectrum obtained with an oxygen doped highly enriched sample of ^{70}Ge . (Courtesy of A.J. Mayur *et al.*)²¹

highest frequency and is readily observed in oxygen rich Ge. High resolution studies show eleven lines, each one split into several components whose intensities depend on temperature. The eleven lines result from the different mass combinations of ^xGe and ^yGe . Combinations with identical linear mass averages (e.g. $^{72}\text{Ge}/^{74}\text{Ge}$, $^{73}\text{Ge}/^{73}\text{Ge}$ and $^{70}\text{Ge}/^{76}\text{Ge}$) lead to the same oxygen vibrational frequencies.

The complexity of such spectra can be reduced very significantly through the use of isotopically pure (or at least highly enriched) crystals. Fig. 4 shows two spectra which were recently reported by Mayur *et al.*²¹ They used oxygen doped natural and four highly enriched Ge crystals. The reduction from eleven to one LVM line is significant because it allows a quantitative study of the line width and of the coupling between v_3 and the other modes as a function of temperature. The splitting is a result of the nonlinear superposition of the v_2 and the v_3 modes. The low frequency v_2 modes can be thermally populated already near liquid helium temperature.

5. Neutron Transmutation Doping (NTD) and Electronic Transport Studies

Lark-Horowitz²² was one of the first solid state scientists who recognized the potential of neutron transmutation doping (NTD). His classical treatise on the topic encompassed all of the interesting nuclear reactions for the semiconductors known at that time. In 1974 the first technological application of NTD of Si was reported by Schnöller.²³ He demonstrated convincingly that the breakdown behavior of high voltage, high power rectifiers occurred over a much narrower range of voltages for n-type silicon produced by the NTD process:

Figure 5. Mobility measured for four differently doped ${}^{74}\text{Ge}:\text{As}$ samples. The theoretically determined mobilities are shown as broken lines²⁷ and continuous lines.²⁵ (Courtesy of K. Itoh *et al.*²⁴)

The availability of highly enriched isotopes of Ge which can be purified to residual dopant levels $<10^{12} \text{ cm}^{-3}$ has provided the first opportunity to measure neutral impurity scattering over a wide temperature range. Itoh *et al.*²⁴ grew a series of high-purity Ge crystals of ${}^{70}\text{Ge}$ and ${}^{74}\text{Ge}$. These crystals were doped with NTD followed by appropriate thermal annealing leading to well defined and ideally homogeneous Ga acceptor and As donor concentrations, respectively. Doping levels between 10^{14} and 10^{16} cm^{-3} with less than 1% compensation were chosen. Fig. 5 shows mobility data points for four n-type ${}^{74}\text{Ge}$ crystals. The continuous lines are not fits to the data but represent the theoretical prediction of the model proposed by Meyer and Bartoli²⁵ with no adjustable parameters. Itoh *et al.* report on infrared absorption linewidth studies of Ga acceptors and As donors in isotopically pure NTD Ge.²⁶

In order to demonstrate the potential of superlattices selectively doped by NTD, let us discuss briefly the formation of a Ge nipi structure.⁵ The necessary donors are created in the neutron transmutation of the ${}^{74}\text{Ge}$ to ${}^{75}\text{As}$ while the acceptors are obtained from ${}^{70}\text{Ge}$ via electron capture and ${}^{71}\text{Ga}$ formation. ${}^{72}\text{Ge}$ and ${}^{73}\text{Ge}$ can be used for the intrinsic layer or to reduce the atomic concentration of ${}^{70}\text{Ge}$ and ${}^{74}\text{Ge}$. Isotopic composition and doping of a hypothetical Ge nipi structure may look like this:

$[{}^{74}\text{Ge}_x:\text{As}/{}^{72} \text{ or } {}^{73}\text{Ge}_{1-x}]:[{}^{72} \text{ or } {}^{73}\text{Ge}]:[{}^{70}\text{Ge}_y:\text{Ga}/{}^{72} \text{ or } {}^{73}\text{Ge}_{1-y}]:[{}^{72} \text{ or } {}^{73}\text{Ge}]: \text{etc.}$
The dopant concentrations after NTD are:

$$[\text{As}] = n_{\text{thermal}} \sigma_{{}^{74}\text{Ge}} x [{}^{74}\text{Ge}] t \quad (10)$$

$$[\text{Ga}] = n_{\text{thermal}} \sigma_{{}^{70}\text{Ge}} y [{}^{70}\text{Ge}] t \quad (11)$$

Isotope superlattices of the other semiconductors offer similar opportunities. Ga self-diffusion in ${}^{69}\text{GaAs}/{}^{71}\text{GaAs}$ isotope superlattices was studied by Tan *et al.*⁴ Elemental heterogeneous superlattices (Si/Ge) as well as homogeneous and heterogeneous superlattices and quantum wells of III-V and II-VI semiconductors can be grown and doped with NTD. Most transmutation products act as donors. This strong

asymmetry in favor of n-type doping can be balanced to some degree by chemical doping during growth with the known shortcomings. A unique aspect of isotope multilayer structures selectively doped via NTD is the option of repeated doping of the same structure. This makes possible doping dependent studies with the identical structure or device.

6. Future Developments and Conclusions

Considering what has been achieved with isotopically controlled diamond and Ge we are confident that a very large number of interesting experiments can be performed if there is enough commitment to obtaining the necessary materials. There can be little doubt that we will see experiments with isotopically controlled Si bulk crystals and perhaps $^{28}\text{Si}/^{30}\text{Si}$ superlattices.

Isotopically controlled III-V and II-VI compound semiconductors and their alloys are most promising in the context of NTD. Zn containing II-VI semiconductors can be doped either with Cu or Ga or not at all, depending on the particular choice of the Zn isotope. The group II partners S, Se or Te offer an abundance of doping possibilities including donors and acceptors. Post-growth doping II-VI semiconductors with the standard techniques (diffusion and ion implantation) has found rather limited success and NTD in combination with isotope control has to be explored as a possible solution to the doping problem.

NTD will play a role in diffusion studies. Self- and impurity-diffusion in a given semiconductor can be studied with superlattices. Sections of the same superlattice can be doped over a broad range of impurity concentrations.

Local vibrational mode studies would become even more powerful than they already are if isotopically controlled host crystals were available. The enormous simplification gained from isotopically pure host crystals has been clearly demonstrated with O in Ge. Just imagine an LVM study of an impurity on the Te site in CdTe. There are five stable Cd isotopes with sizable atomic fractions leading to a very large number of neighbor mass combinations!

Nuclear reactions with isotopes offer a range of opportunities which have not been explored. Other opportunities exist with electron paramagnetic spin resonance techniques which make use of the interactions between electron and nuclear spins. Isotope control and engineering of semiconductors and other solids offers almost limitless possibilities for solid state studies and novel devices. This post cold war era has brought great opportunities for making highly enriched isotopes more readily available to the science and technology community.

7. Acknowledgments

I am indebted to many colleagues who have collaborated with us on studies of isotopically controlled Ge. I can only list a small number of the major contributors and I sincerely apologize whose names I cannot include because of space limitations. The field was advanced significantly by G. Abstreiter, M. Cardona, G. Davies, H. Fuchs, W. L. Hansen, K. M. Itoh, V. Ozhogin, A. K. Ramdas and W. Walukiewicz.

This work was supported in part by the Lawrence Berkeley Laboratory Directed Research and Development Program through US DOE contract DE-AC03-76SF00098, and in part by the US National Science Foundation Center for Particle Astrophysics contract ADT-8809616.

8. References

1. T.H. Geballe, and G. Hull, Phys Rev. **110**, 773 (1958).
2. I. Pomeranchuk, J. Phys. (Moscow) **6**, 237 (1942).
3. E.E. Haller, Infr. Physics & Technology **35**, 127 (1994).
4. T.Y. Tan, H.M. You, S. Yu, U. Gösele, W. Jäger, D.W. Boeringer, F. Zypman, R. Tsu, and S.-T. Lee, J. Appl. Phys. **72**, 5208 (1992).
5. E. E. Haller, Semic. Sci. and Techn. **5**, 319 (1990).
6. Kohei Itoh, W. L. Hansen, E. E. Haller, J. W. Farmer, V. I. Ozhogin, A. Rudnev and A. Tikhomirov, J. Mat. Res. **8**, 1341 (1993).
7. W.F. Banholzer and T.R. Anthony, Thin Solid Films **212**, 1 (1992).
8. M. Cardona, these proceedings.
9. G. Davies, E.C. Lightowers, K. Itoh, W.L. Hansen, E.E. Haller and V. Ozhogin, Semic. Sci. and Techn. **7**, 1271 (1992).
10. Gordon Davies, E.C. Lightowers, T.S. Hui, V. Ozhogin, K. Itoh, W.L. Hansen and E.E. Haller, Semiconductor Science and Technology **8**, 2201 (1993).
11. H. Holloway, K.C. Haas, M.A. Tamor, T.R. Anthony, and W.F. Banholzer, Phys. Rev. B **44**, 7123 (1991).
12. A.K. Ramdas, S. Rodriguez, M. Grimsditch, F.R. Anthony, W.F. Banholzer, Phys. Rev. Lett. **71**, 189 (1993).
13. Lanhua Wei, P.K. Kuo, R.L. Thomas, T.R. Anthony, and W.F. Banholzer, Phys. Rev. Lett. **70**, 3764 (1993).
14. V.F. Agekyan, V.M. Asnin, A.M. Kryukov, I.I. Markov, N.A. Rud', V.I. Stepanov, and A.B. Churilov, Sov. Phys. Solid State **31**, 2082 (1989).
15. P. Etchegoin, J. Weber, M. Cardona, W.L. Hansen, K. Itoh, and E.E. Haller, Sol. State Comm. **83**, 843 (1992).
16. S. Zollner, M. Cardona, and S. Gqsalan, Phys. Rev. B **45**, 3376 (1991).
17. C. Parks, A.K. Ramdas, S. Rodriguez, K.M. Itoh and E.E. Haller, Phys. Rev. B **49**, 14244 (1994).
18. M. Cardona, P. Etchegoin, H.D. Fuchs, P. Molinàs-Mata, J. Phys.: Condensed Matter **5**, A61. (1993).
19. B. Jusserand and M. Cardona, in *Light Scattering in Solids*, eds. M. Cardona and G. Güntherodt (Springer, Heidelberg, 1989), Vol. V, p. 49.
20. W.G. Spitzer, these proceedings.
21. A.J. Mayur, M. Dean Sciacca, M.K. Udo, A.K. Ramdas, K. Itoh, J. Wolk, and E.E. Haller, Phys. Rev. B **49**, 16 293 (1994).
22. K. Lark-Horowitz, Proc. Conf. on Semi-Conducting Materials, H.K. Henish, ed. (Butterworth Sci. Publ., London, 1951) pp. 47-69.
23. M.S. Schnöller, IEEE Trans. Electr. Dev. **ED-21**, 313 (1974).
24. K. M. Itoh, W. Walukiewicz, H. D. Fuchs, J. W. Beeman, E. E. Haller, J. W. Farmer and V. I. Ozhogin, "Neutral Impurity Scattering in Isotopically Engineered Ge," subm. to Phys. Rev. B.
25. J. R. Meyer and F. J. Bartoli, Phys. Rev. B **24**, 2089 (1981).
26. K.M. Itoh *et al.*, Proc. 6th Intl. Conf. on Shallow Level Centers in Semiconductors, Berkeley, Aug. 10-12, 1994, to be published in Solid State Comm.
27. C. Erginsoy, Phys. Rev. **79**, 1013 (1950).