ULTRASONIC SPECTROSCOPY OF THE

ACCEPTOR GROUND STATE IN CUBIC SEMICONDUCTORS

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INTRODUCTION

Phonons are effectively scattered by electrons and holes bound to donors and acceptors in semiconductors at low temperatures corresponding to the relatively large deformation potential constants involved. This has been found over twenty years ago in measurements of the thermal resistivity and the ultrasonic attenuation of bound donor states in Germanium. Since then many phonon scattering experiments on both donors and acceptors have been carried out and a lot of results have been obtained[1]. Much of the progress in understanding is due to the progress of industry and research in manufacturing pure and well-defined crystals. This applies particularly to the acceptor ground state which is very sensitive to crystal imperfection. In the following we will discuss ultrasonic measurements on p-type semiconductors reflecting spontaneous and defect sensitive modifications of the acceptor ground state.

For the bound states of shallow impurities in semiconductors a hydrogenic model is justified where the wavefunctions are constructed from the neighbouring band states leading to relatively small ionization energies $E_A \simeq 10$ to 100 meV and relatively large Bohr radii $r_B \propto 1/\sqrt{E_A} \sim 100$ to 10 Å. This means that these states are extended point defects. The ground state of acceptors in cubic semiconductors is a fourfold degenerate Γ_8 state that may be split by elastic or electric fields into two Kramers doublets. A magnetic field will lift the degeneracy completely. Such a Γ_8 state should, in principle, show an instability against spontaneous deformation, viz. a Jahn-Teller effect. However, because of the extended wavefunction, a Jahn-Teller effect is expected to be weak for shallow acceptors, it

should be more pronounced for deeper acceptors with their smaller Bohr-radii.

In fact, for two acceptors, namely GaAs(Mn) (E_A=110 meV, r_B=10.4 Å) and Si(In) (E_A=156 meV, r_B=7.3 Å) we have found resonance energies at 3.1 meV and 4.2 meV respectively, in reasonable accordance with first calculations of the problem[2]. Experimentally, these values have been obtained from an analysis of the ultrasonic relaxation attenuation[3] [4], from thermal conductivity measurements[5], and, in the case of Si(In), also from experiments with quasimonochromatic phonons[6] and from a satellite in luminescence[7].

The vibronic ground state of the system will exhibit full symmetry, that is, it will also be a Γ_8 state. Internal elastic and electric fields originating from crystal defects will lead to a distribution of splittings which,in turn, may be regarded as an indicator of residual defects. Such a distribution of two-level systems is quite analogous to that encountered in glasses, and we are faced with the same problems as to the form of the distribution, the relaxation times and the interaction between defects.

THE DISTRIBUTION OF SPLITTINGS

The form of the distribution function may be obtained by measuring the resonant attenuation in a wide frequency range: Since the attenuation α is proportional to the spectral density $N(\delta)$ of the splittings δ at a certain frequency $\nu=\delta/h$, the distribution is thus probed in the corresponding frequency range.

For the resonant absorption we have

$$\alpha(\nu,T) = \int N(\delta)\alpha(\delta,\nu,T)d\delta$$

$$\alpha(\nu,T) \propto \int\left[\tanh(\delta/2kT)D^2_{eff}(\delta)N(\delta)\nu\Gamma(\delta,T)/\left[(h\nu-\delta)^2+\Gamma^2(\delta,T)\right]\right]d\delta$$

If the linewidth $\Gamma(\delta,T)$ of the resonance line is small enough compared to the variation of $N(\delta)$, $D_{eff}(\delta)$ we can write:

$$\alpha(\nu,T) \propto \left[N(\delta=h\nu)D^2_{eff}(\delta=h\nu)\right](\nu^2/T)$$

for $h\nu \ll kT$. The effective coupling constant D_{eff} is a combination of the two well-known deformation potential constants of the ground state corresponding to the "average" symmetry of the disturbing field. Assuming that this "average" symmetry does not vary with δ we may write $\alpha(\nu)/\nu^2 \propto N(\delta=h\nu)$ at a fixed temperature. In Fig.1 we have plotted the variation of $\alpha(\nu)/\nu^2$ in the frequency range 0.5 GHz$\leq\nu\leq$4.2 GHz for a boron doped high quality silicon crystal. Under the assumption that D_{eff} is constant and that $\alpha(\nu)/\nu^2$ is negligibly small outside our measuring range we can integrate the
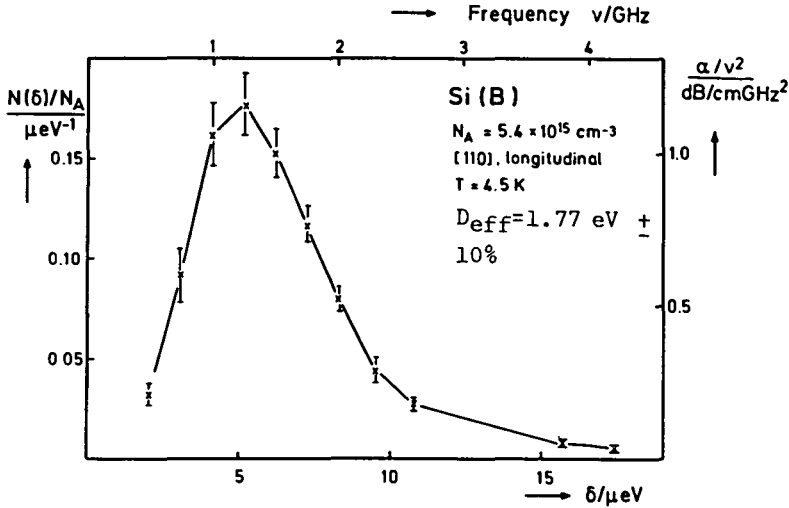
Fig. 1: Distribution of splittings of the boron acceptor ground
        state for a high quality silicon crystal.

area to obtain $N_A \cdot D_{eff}^2$ where N_A is the known acceptor concentration.
The value $D_{eff}=1.8$ eV seems reasonable in comparison with the two
deformation potential constants $D_u^a = 2.4$ eV and $D_u^{a'} = 3.9$ eV. In
applying uniaxial pressure we have verified for a similar crystal
that there is no peak in the distribution function at $\delta=0$. Measuring
the attenuation for other directions and polarizations one may sepa-
rate the different elastic constants involved to get additional
information on D_{eff}. In Fig. 2 the distribution functions are shown
for a series of high quality silicon crystals of varying boron con-
centrations. They are all similar with maxima between 1 GHz and 2
GHz, falling rapidly off at low frequencies. With growing boron
concentration there is a tendency to flatten the maximum and to
broaden the distribution to higher energies. All these crystals
(supplier Wacker Chemitronic, Burghausen, F.R.G.) are floating
zone-pulled, dislocation-free, with low carbon and oxygen
contents (below 10^{15} cm^{-3} to 10^{16} cm^{-3} typically). The
pulling velocity was high enough to avoid detectable clusters of
selfinterstitials ("swirl-free" crystals), however, the concentra-
tion of selfdefects is unknown. It may be as high as 10^{17} cm^{-3}.
(The concentration of selfdefects may be reduced in pulling the
crystal at extremely low velocity, where the defects have time to
diffuse out of the crystal during growth[8]). The crystal of Fig. 1
differed from those of Fig. 2 in that the pulling conditions were
such as to produce an even higher homogeneity of the crystal.

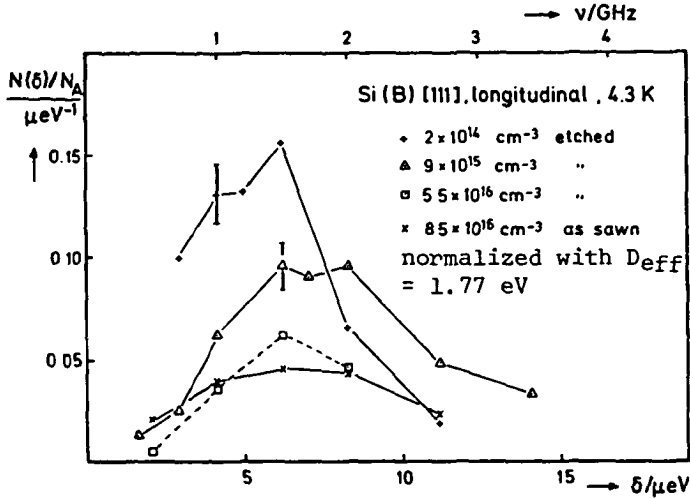In less pure crystals (Czochralski-grown Si(B) and Si(In) with

Fig. 2: Distribution of splittings for various boron concentrations.

high carbon and oxygen content) we find only a rise in α/ν^2 indicating a maximum beyond our limit of about 4 GHz. Earlier we have found for GaAs($\sim 10^{18}$ cm^{-3} Mn) [3] α/ν^2 to be practically constant from 0.4 to 2.0 GHz and also for Ge of various doping[9] between 8×10^{15} cm^{-3} and 3×10^{16} cm^{-3} α/ν^2 constant between 1.2 GHz and 2.5 GHz indicating a width of the distribution of about 50 µeV and 100 µeV respectively. (In contrast, for a very pure Ge(2×10^{14} cm-3 Ga) crystal grown and kindly supplied by E.E. Haller of Lawrence Berkeley Laboratory, California, we find a distribution even narrower than that of Fig. 1 with maximum near 1 GHz.)

So far, we don't know the reason for the residual linewidth of the purest crystals. We shall shortly discuss three possibilities: (i) Though there is some correlation with boron concentration visible in our results, ground state splitting due to wave function overlap seems improbable, since we would expect a monotonous exponential dependence of the splitting on mean acceptor distance for this range of small energies[10] . (ii) Electric fields from residual compensating donors should be too small for the low concentrations of residual donors ($\sim 10^{12}$ cm^{-3} in the purest crystal). In Ref. 11 we overestimated the electric field in our calculation. Furthermore, at low temperatures the ionized donors and acceptors should not be uncorrelated, as assumed[12] in that calculation, because a nearest neighbour correlation will be energetically more favourable. Such a correlation will lead to a further reduction of the electric field, as we have found by a computer simulation. (iii) Strain fields from point defects would be expected at relatively high concentrations. In Fig. 3
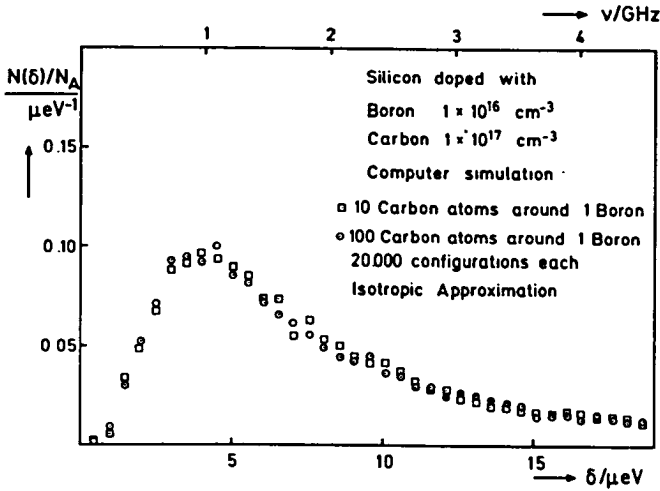
Fig. 3: Computer simulation of splitting distribution due to
        substitutional carbon.

we have plotted the distribution of splitting resulting from a com-
puter simulation for substitutional carbon with an elastic strength
$A = -0.85 \text{ Å}^3$ corresponding to its covalent radius in an isotropic
approximation for the crystal. Since the elastic strength of boron
is much smaller, we see that neither the boron nor the carbon or
oxygen content should be responsible for the residual splitting.
Since the concentration of intrinsic defects or their agglomeration
is unknown, at the present state of our investigation we cannot say
whether selfdefects or some other defects or perhaps some effects
intrinsic to the isolated acceptor are responsible for the residual
splitting.

THE CRITICAL INTENSITY

        To separate the resonant attenuation α_{res} from relaxation
attenuation and geometrical effects we make use of the possibility
of saturation at high acoustic intensities. From these intensity
dependent measurements we obtain the critical intensity J_c.

        In a Bloch equation formalism we obtain from J_c the product
$\tau_1 \cdot \tau_2$ of the "spin"-lattice or energy relaxation time τ_1 and the
transverse or dephasing relaxation time τ_2

$$J_c \propto 1/(\tau_1 \cdot \tau_2)$$

If only "spin"-lattice relaxation were effective, one might assume

$\tau_1 \cdot \tau_2 = 2\tau^2$ [13] ; i.e. I_c should not depend on N_A. A dynamical inter-
action between the acceptors should shorten τ_2, leading to a larger
I_c for smaller mean distances between the acceptors. In Fig. 4 we
have plotted the critical intensity for various acceptor concentra-
tions. We see that below about 10^{16} cm^{-3} the critical intensity does
not depend on N_A. From $I_c \approx 10^{-4}$ W/cm^2 we estimate $\tau_1 \cdot \tau_2 / \sqrt{2} = \tau_1 =$
1.4×10^{-8} sec, whilst from our measurement of the relaxation attenua-
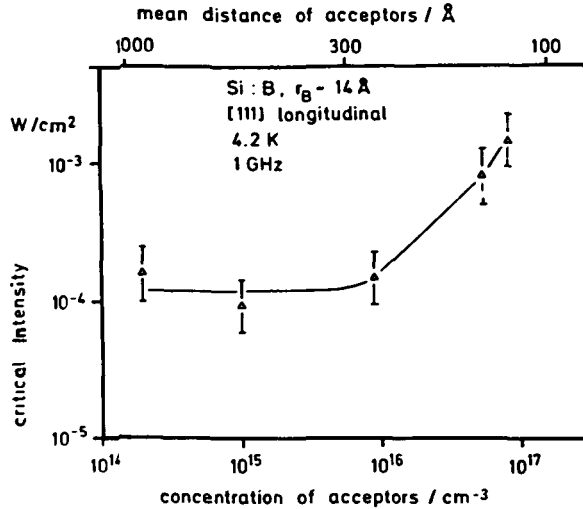

Fig. 4: Critical intensity as a function of average acceptor
        distance.

tion we have $\tau_1 = 1.3 \times 10^{-8}$ sec, which means, that for average dis-
tances larger than about 300 Å the critical intensity is determined
by "spin"-lattice relaxation alone. For smaller distances d the
critical intensity rises roughly as $1/d^3$, as one might expect for
a dipolar interaction[13][14]. However, applying the formula for spec-
tral diffusion by elastic dipolar interaction given in 14 for our
experimental conditions (Raman/Orbach relaxation, narrow distribu-
tion), we arrive at $\Delta\omega/Hz = 5.6 \cdot 10^{-8}$ (N_A/cm^{-3}) (independent on tem-
perature) which leads to τ_2 being too small by an order of magni-
tude. Also the temperature dependence of J_c varies more slowly than
expected. We are, therefore, preparing experiments for a direct
determination of τ_2.

    Applying uniaxial pressure will "shift" the distribution and
reduce the concentration of acceptors on speaking terms. In our
first experiments we have seen no effect on I_c at 4.2 K reducing

$\alpha(\nu)/\nu^2$ by about a factor of five. This is as expected since the energy-independent Raman/Orbach relaxation is dominant in this range so that spectral diffusion should remain unchanged and on the other hand because the acceptors on speaking terms are at any rate relatively minor in number to have an influence on spectral diffusion.

For the narrow distribution in a magnetic field acoustic paramagnetic resonance can be seen and lines be resolved at 4 GHz. Also EPR at 10 GHz is possible in these clean crystals, as was recently shown[15]. By detailed investigation of the APR at somewhat higher frequencies we should get additional information on the symmetry and distribution of the random splittings of the acceptor ground state.

We hope that investigations of this kind may help to some practical informations concerning residual crystal defects as well as to a better understanding of the dynamical processes connected with the two-level systems.

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DISCUSSION

R. Collella: These impurities are on the average inhomogeneously
distributed in these crystals. I was wondering whether you have
considered using crystals like silicon in which the doping is
achieved by neutron irradiation, and you can have the same kind of
doping with the same percentages, but you are sure that it is much
more homogeneous. It would be interesting to compare if you get the
same results.

K. Lassmann: By this method you can obtain donors by transportation
of silicon into phosphorous, and this we used already in one case.
For acceptors I don't know of a possibility to make it more homo-
geneous. What we tried to do was to look with an infrared micro-
scope and in the case of some silicon-indium crystals where we also
have some broader distribution there we saw some striations. With
these silicon crystals, especially the first one I showed, it would
be very inhomogeneous, the suppliers told me but they didn't tell me
how they told it. There we didn't see with the microscope any
striations, but we cannot tell any more about that. What we want
to do is to see if there is any inhomogeneity correlated say with
the pulling direction so we might work in different directions if we
are allowed to do it. For instance, under pressure we could see
whether there are three types of strain. This is really a problem.
Also association between defects might be a problem.

J. P. Harrison: Could you measure the strain dipole moment by
applying a stress and then repeating your measurements?

K. Lassmann: It is potentially given by the deformation potential
constants which have been measured.