

in the conduction electron concentration by a factor 10. Thus it can be seen that the resonance is not wholly due to conduction electrons as long as some electrons remain bound to the donor nuclei. It may therefore be difficult to interpret line widths and line shapes, especially in the impurity scattering region.

On the basis of Elliott's theory there should be no change of line widths with electron concentration, in the lattice scattering region, unless Δg varies appreciably with concentration. Up to the present it has not been possible to measure g -values to the necessary degree of accuracy, because of the presence of the surface state resonance. There is a possibility that even at elevated temperatures an impurity relaxation mechanism is responsible, in part at least, for the observed line width. The width due to such a mechanism would presumably increase with increasing impurity concentration.

Future experiments will be carried out with the aim of investigating the line width at lower temperatures, and to ascertain whether the g -value is dependent on the impurity concentration.

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N 4 Spin-Lattice Interaction for Electrons in Semiconductors

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The direct spin lattice interaction for electrons in semiconductors can be described as the modulation of the electron's g -tensor by the lattice vibrations. For a donor state in Si, there is a contribution due to the mixing in of the doublet excited state by the deformation, and one due to the change in the g -tensor in one valley. The relative importance of the two terms will be discussed and compared with experiment.

In this paper the direct spin lattice relaxation time is calculated for electrons in semiconductors, in particular, for donor electrons in silicon. The first attempts to calculate this, by PINES, BARDEEN and SCHLICHTER [1] and by ABRAHAMS [2]

*) Operated with support from the US Army, Navy, and Air Force.

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failed to account for the relaxation rate. Recently the author [3] and HASEGAWA [4] proposed a mechanism which more than accounted for the size of the interaction but which gave the wrong anisotropy. This paper extends the work of these authors. We treat here only the silicon problem; the approach can however be applied to semiconductors generally.

The unperturbed system is an electron in a donor state and subject to a magnetic field. As is well known, the donor state is split by the valley-orbit interaction into a singlet ground state, and doublet and triplet excited states. These are made up of linear combinations of donor states on each of the six valleys. The electron spin's interaction with the magnetic field \mathbf{H} is modified by spin orbit interaction, and near the conduction band edge on a given valley, this is described by a \mathbf{g} -tensor. Thus for the i 'th valley

$$(1) \quad \mathcal{H}_{si} = \frac{\beta}{2} \boldsymbol{\sigma} \cdot \mathbf{g}_i \cdot \mathbf{H}.$$

From symmetry \mathbf{g}_i has only components g_{\parallel} and g_{\perp} , parallel and perpendicular to the directions of the valley. Expressions have been obtained for these [3] by a method analogous to that for the effective masses. We shall assume that for the impurity state the \mathbf{g} -tensor is the same as that for the band edge. The impurity contribution to the \mathbf{g} -shift appears to be small [2]. For the actual donor state we then average over the various valleys:

$$(2) \quad \mathbf{g} = \sum_i C_i^2 \mathbf{g}_i,$$

where C_i are the coefficients in the linear combination. For the unperturbed singlet state, $C_i = 1/\sqrt{6}$, and the \mathbf{g} -tensor is a simply the scalar $g = \frac{1}{3}g_{\parallel} + \frac{2}{3}g_{\perp}$.

We now add the electron-phonon interaction as a perturbation. For long wave length acoustical phonons we use a generalization of the deformation potential:

$$(3) \quad \mathcal{H}_d = \boldsymbol{\epsilon} : \mathbf{E}(\mathbf{r}, \mathbf{p}),$$

where $\boldsymbol{\epsilon}$ is the strain tensor for the lattice deformation, and the tensor \mathbf{E} is an operator in the electronic coordinate \mathbf{r} and momentum \mathbf{p} . \mathbf{E} has the periodicity of the lattice, and we shall make use of its interband as well as its intra-band matrix elements at the band edge. The use of Eq. (3) can be justified if various small terms are neglected.

The "spin flip" matrix element of \mathcal{H}_d would vanish in the absence of spin orbit interaction. If we include the latter as a perturbation, we have an effective interaction depending on the strain tensor $\boldsymbol{\epsilon}$ and the spin vector $\boldsymbol{\sigma}$. However $\boldsymbol{\sigma}$ changes sign under time reversal, and to make the interaction time reversal invariant we must include the magnetic field \mathbf{H} in the expression. For the

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donor state which has tetrahedral symmetry the form of the interaction is then

$$(4) \quad \mathcal{H}'_d = A\beta(\sigma_x\epsilon_{xx}H_x + cp - \sigma \cdot \mathbf{H} \Delta/3) + \\ + B\beta(\epsilon_{xy}(\sigma_xH_y + \sigma_yH_x) + cp) + C\beta\sigma \cdot \mathbf{H}\Delta,$$

where Δ is the dilitation and cp stands for "cyclic permutations". Here we can neglect the spatial variation of ϵ over the impurity state, since the wavelength of the phonons is long. The last term does not flip spins, and so can be ignored. If we compare Eq. (4) with Eq. (1), we see that the spin lattice interaction due to \mathcal{H}'_d can be regarded as a modulation of the electron's \mathbf{g} -tensor by the deformation. We can therefore simply calculate the electron's \mathbf{g} -tensor in the deformed crystal.

The effect of the deformation is to change both C_i and \mathbf{g}_i in Eq. (2). The change in C_i is due mainly to the change in energy of the band edges; the matrix element of \mathcal{H}'_d between donor states on valleys i and j is then

$$(5) \quad \langle i|\mathcal{H}'_d|j\rangle = \{E_1\Delta + E_2(\mathbf{n}_i \cdot \boldsymbol{\epsilon} \cdot \mathbf{n}_i - \Delta/3)\} \delta_{ij},$$

where E_1 and E_2 are the ordinary deformation potential parameters [6] and \mathbf{n}_i is a unit vector in the direction of the valley. \mathcal{H}'_d has a matrix element between the ground state and the doublet, so that by perturbation theory this "singlet-doublet" interaction is found to be of the form (4) with

$$(6) \quad A_1 = \frac{(g_{||} - g_{\perp})}{3} \frac{E_2}{\delta}; \quad B_1 = 0,$$

where δ is the singlet-doublet splitting.

The change in \mathbf{g}_i , which now has more than two components, can be calculated from perturbation theory using the interband matrix elements of \mathcal{H}'_d . The result is a fourth order expression analogous to that for the \mathbf{g} -tensor ([3], Eq. (10)). The largest terms are found to be those involving the Δ'_2 band edge, which is close to the Δ_1 conduction band edge, closer in fact than Δ_5 which appears in the expression for the transverse effective mass. The result for this one-valley interaction is again of the form (4), with now, however,

$$(7) \quad A_2 = 0; \quad B_2 = \frac{2i\beta}{3m} \frac{(\Delta_{2'}|p_z|\Delta_{2'})(\Delta_{2'}|E_{xy}|\Delta_1)}{\epsilon_{12}^2\epsilon_{15}} \cdot \\ \cdot \{(\Delta_1|p_x|\Delta_5^x)(\Delta_5^x|h_x|\Delta_{2'}) + (\Delta_1|h_x|\Delta_5^y)(\Delta_5^y|p_x|\Delta_{2'})\},$$

where $\sigma \cdot \mathbf{h}$ is the spin orbit operator, and the matrix elements and energy denominators are between the band edges mentioned above, for an (001) valley. The matrix elements are similar to those found in the calculation of the g_{\perp} -shift, Δg_{\perp} , so that by comparing the two we find

$$(8) \quad B_2 \sim \Delta g_{\perp} \frac{\epsilon_{15}}{\epsilon_{12}^2} (\Delta'_2|E_{xy}|\Delta_1).$$

Given the spin lattice interaction, Eq. (4), one can calculate the spin lattice

relaxation time in an isotropic material

$$(9) \quad \tau_s^{-1} = \frac{1}{\pi} \frac{\omega^2}{g}$$

where g is the velocities. The temperatures (field) are both and STUPP [8] depending on by FEHER [9] direction. Put $5 \cdot 10^{-4} \text{ sec}^{-1}$ assume that $\sim 4 \text{ eV}$, and for the impurity contribution from $B = 2$. estimate would in fact in the or singlet-doublet overestimates. The solution of FEHER [9] be much smaller and thus appear.

As has been Eq. (8), can be \mathbf{g} -tensor. It should be when non-

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The author with Dr. H. F.

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relaxation time τ_s for low temperatures by standard methods [1-4]. Using an isotropic model for the lattice vibrations, the result is

$$\tau_s^{-1} = \frac{1}{\pi} \frac{\omega^4 kT}{g^2 \rho} \left[\frac{2}{5c_t^5} + \frac{4}{15c_l^5} \right] \left\{ A^2 \left(\frac{H_x^2 H_y^2 + cp}{H^4} \right) + B^2 \left(\frac{1}{2} - \frac{H_x^2 H_y^2 + cp}{H^4} \right) \right\}, \quad (9)$$

where ρ is the density and c_t and c_l are the transverse and longitudinal sound velocities. The linear dependence on the temperature T for sufficiently low temperatures, and the quartic dependence on the frequency ω (i. e. the magnetic field) are both in agreement with the results of FEHER and GERE [7] and HONIG and STUPP [8]. We see that τ_s is predicted to be anisotropic, with the anisotropy depending on the relative values of A and B . An anisotropy has been observed by FEHER [9] with τ_s 50% longer for H in the [100] direction than in the [111] direction. Putting numbers in, the factor in front of the curly bracket is $5 \cdot 10^{-4} \text{ sec}^{-1}$ for Si at 1.2°K and 9000 Mc/s. In estimating A and B , if we assume that $(\Delta_1 | E_{xy} | \Delta_2) \sim E_2 = 11 \text{ eV}$, $\delta = 0.01 \text{ eV}$, $\epsilon_{12'} \sim 0.6 \text{ eV}$, $\epsilon_{15} \sim 4 \text{ eV}$, and that the factors involving g_{\parallel} and g_{\perp} are of the order of the g -shift for the impurity, $\Delta g = 0.003$, we obtain $A^2 \sim 10^1$ and $B^2 \sim 10^{-1}$. Then the contribution to τ_s^{-1} from A , for an average direction of H , is 10^{-3} sec^{-1} , and from $B = 2 \cdot 10^{-5} \text{ sec}^{-1}$. The experimental result is about 10^{-5} sec^{-1} . This estimate would indicate that the singlet-doublet interaction dominates. In fact in the original calculations [3, 4] only this term was calculated, since the singlet-doublet splitting is much smaller than an energy gap. However, this overestimates the relaxation rate and predicts too large an anisotropy in τ_s . The solution to this puzzle appears to be found in recent experimental results of FEHER [9] in which the anisotropy in the g -tensor, $g_{\parallel} - g_{\perp}$, was found to be much smaller than the g -shift; this result reduces the contribution from A , and thus appears to produce agreement with experiment.

As has been pointed out by FEHER [9], the form of the effective interaction, Eq. (8), can be investigated by measuring the effect of static strains on the g -tensor. It should be possible to distinguish the two mechanisms on the basis of when non-linearity sets in for large strains.

Acknowledgement

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N 5 Interactions Between Impurities in Silicon

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An improved understanding of silicon doped with transition metal ions has resulted from electron spin resonance measurements. The ions of the 3d group are normally interstitial and diffuse at room temperature. They combine with vacancies, becoming substitutional, and also associate with acceptor ions, forming donor-acceptor pairs.

Although it is one of the best understood semiconductors, little was known about silicon doped with transition metal ions until recently. The solubilities of a few ions had been measured, and fragmentary information was available about diffusion rates and electrical behavior. There was little information about the sites occupied by the ions, or about their electronic structure. Our understanding of such systems has increased considerably in the past several years largely as a result of spin resonance measurements [1].

A number of transition metal ions can be introduced into silicon by diffusion at 1300°C. The solubility at 1300°C is close to its maximum value, typically $\sim 10^{16}$ atoms/cm³. Samples are quenched to keep the ions dispersed in the lattice. Their charge state can be controlled by using starting material doped suitably with a donor or an acceptor impurity. Despite the modest band gap of silicon (~ 1.2 eV), multiple charge states are found. For example, manganese can be introduced interstitially as Mn⁺⁺, Mn⁺, Mn⁰, and Mn⁻, and substitutionally as Mn⁺, Mn⁰, Mn⁻, and Mn⁻⁻. Six of these eight species have been detected by spin resonance.

The ions of the 3d group are interstitial in crystals doped as described above. Properties of crystals containing them change with time, corresponding to the large diffusion constant of the ions ($\sim 10^{-15}$ cm²/sec at room temperature). Experiments in which the ions trap vacancies, thereby becoming substitutional, furnish further evidence of their interstitial character. The vacancies can be introduced, chemically, by diffusing an impurity like copper into the sample. Copper is quite soluble ($\sim 10^{18}$ atoms/cm³) at 1300°C. When the sample is

cooled it precipitates vacancies can trap electrons.

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