DIRECT MEASUREMENT OF THE VALLEY-ORBIT SPLITTING OF SHALLOW DONORS IN SILICON

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This Letter reports the determination of valley-orbit splittings for phosphorus, arsenic, antimony, and bismuth donors in silicon by the measurement of the temperature dependence of the spin-lattice relaxation rate from 4.2°K to 33°K. The spin-lattice relaxation rate at sufficiently high temperatures depends exponentially on Δ/kT, where Δ is the valley-orbit splitting. Reported here are the first accurate values of the valley-orbit splittings for shallow donors in silicon. In addition, the results for arsenic suggest the possible importance of Umklapp-type intervalley scattering on the relaxation rate. This would be the first indication of Umklapp intervalley scattering at such low temperatures.

Kohn and Luttinger[1] first pointed out that the degeneracy of the donor ground state is lifted by the impurity potential. Spin resonance experiments in Si[2] and Ge[3] have confirmed this splitting. Hall effect measurements[4] have shown this splitting for P-doped Si to be between 0.009 and 0.012 ev. Recently, uniaxial strain experiments[5] have been used to determine the ratio of the uniaxial shear deformation constant, Ξ_u, to Δ, the valley-orbit splitting. Hasegawa[6] and Roth[7] have used a perturbation theory treatment of the spin-lattice relaxation rate in which phonons, through the uniaxial shear deformation potential, mix the low-lying 1S doublet states with the 1S singlet ground state. The theory gives excellent agreement with experimental results for the single-phonon process.[5,8] An exponential temperature dependence for spin-lattice relaxation was first suggested by Lloyd and Pake[9] and first found for Ce^{+++} in $Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$.[10] Orbach[11] has treated the rare-earth–ion case theoretically. In the rare-earth–ion case the small splitting is due to the removal of the degeneracy of the J_z states by the crystalline field. In silicon the sixfold degeneracy due to six conduction band minima is split by the impurity potential, giving a singlet, doublet, and triplet for each hydrogenic donor state.

Relaxation time measurements were made with an X-band spectrometer using bolometer detection, a narrow band amplifier, and recorder for steady-state measurements. Transient measurements were made by converting the spectrometer to a single klystron phase-sensitive superheterodyne system with scope display. The sample cavity was enclosed in a vacuum-tight can containing exchange gas. A heater coil was wound around the copper cavity, which was insulated from the refrigerant reservoir temperature by stainless steel guide. With the heater the temperature range between 4.2°K and 11°K and between 20.3°K and 33°K could readily be covered.

The spin resonance lines are Gaussian in shape as a result of inhomogeneous broadening.[2] The absorption susceptibility saturation behavior agrees with Portis' theory[12] for the case that the spin packet width is due to the spin-lattice relaxation time, T_1. The onset of saturation is then a direct measure of T_1. For T_1 less than 3×10^{-8} second, the Gaussian envelope was observed to broaden

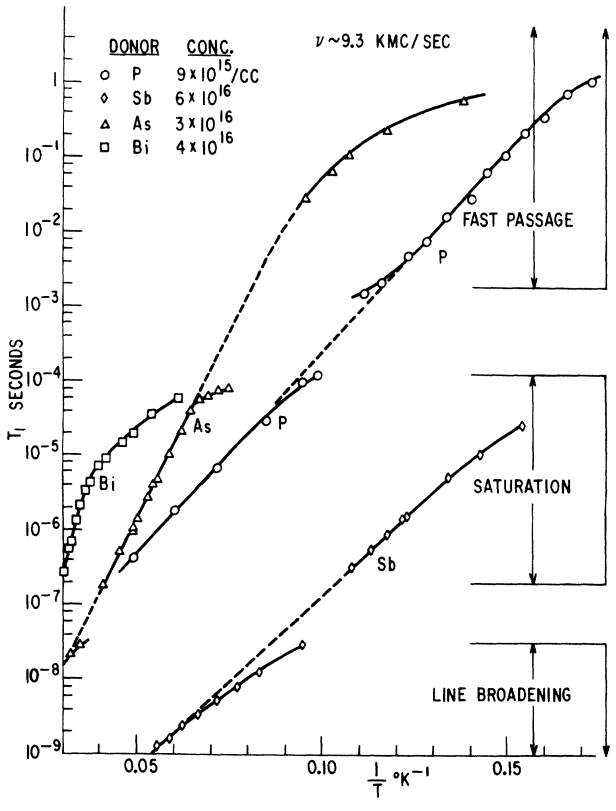

FIG. 1. The temperature dependence of the spin-lattice relaxation time, T_1, for donor electrons in silicon. Below the exponential temperature region $1/T_1 \propto T^n$, with $n \sim 7$ to 9.

and gradually change to a Lorentzian shape. Measuring the width as the line broadens at high temperatures gives a direct measure of T_1. For times longer than 10^{-3} second, a variety of adiabatic fast passage methods was used to obtain T_1's.

Figure 1 shows $\log T_1$ versus $1/T$ for P, As, Sb, and Bi. The P and Sb show exponential relaxation ($1/T_1 = Re^{-\Delta/kT}$) above 6°K; As exhibits exponential relaxation above 11°K; while Bi gives exponential relaxation above 26°K. The slopes in the temperature range where the relaxation is exponential give the valley-orbit energy splittings for the different donors. The results are shown in Table I. If one adds the Δ values to the experimental optical ionization energies, E_0, one finds the energy of the 1S doublet (and triplet) relative to the conduction band minimum. It is noted that this level is closely the same for all the donors within the experimental accuracy. The Bi result is not very accurate because the exponential relaxation could only be measured over a narrow range of $1/T$. The result that the 1S doublet (and triplet) energy level is independent of the donor suggests that these states obey effective-mass theory quite well, as is expected since the wave functions describing these states have zero probability density at the donor nucleus. However, the energy is depressed about 5×10^{-3} ev below Kohn and Luttinger's calculated value[1] of -29×10^{-3} ev based on effective-mass theory. It is suggested that this lower energy is due primarily to the breakdown of the continuum dielectric constant for the first shell or two of silicon atoms surrounding the donor rather than to the impurity potential. A lower dielectric constant for the first shell region would lower the energy levels by an amount which would be independent of the donor.

The phonons responsible for this exponential relaxation have approximately the energy Δ; hence the phonon wave number $q_\Delta = \Delta/\hbar v$, where v is the velocity of sound and $\hbar$ is Planck's constant. Because the phonon wavelength is small compared to the donor orbits ($q_\Delta r \gg 1$, where r is the donor orbit radius), the long-wavelength approximation is bad, and the intravalley orbit-lattice interaction is greatly reduced by interference. Furthermore, for phonons with energy Δ the longer wavelength longitudinal phonons become more important for relaxation than transverse phonons. Intervalley scattering via Umklapp to the opposite valley ([100] to [100]) can be important for q_Δ's close to q_u, the wave number required for Umklapp. For silicon $q_u = 0.30\, q_{\max}$ ($q_u = 0.345\times10^8$ cm^{-1}) since the conduction band minima are 15% in from the zone edge on [100] axis.[2] For phosphorus $q_\Delta = 0.19\times10^8$ cm^{-1}, while for arsenic $q_\Delta = 0.34\times10^8$ cm^{-1} for longitudinal phonons propagating along a [100] axis. Preliminary calculations have indicated the dominance of the intervalley Umklapp process for As and show the orbit-lattice coupling between the singlet and the valley states[13] to be much larger for As than for P, allowing one to explain the large

Table I. Valley-orbit splitting for shallow donors in silicon, 1S doublet and triplet (D & T) energy levels, uniaxial shear strain deformation potential constant, and spin-lattice relaxation rate constants ($1/T_1 = Re^{-\Delta/kT}$).

Donor	Conc. (n/cc)	R (10^{10} sec^{-1})	Δ (10^{-3} ev)	E_0 (10^{-3} ev)	$E_{1S,\,D\&T}$ (10^{-3} ev)	Ξ_u ev
P	9×10^{15}	0.071	10.6 ± 0.2[b]	-44.6[b,c]	-34.0[b]	8.0[f]
P[a]	4×10^{15}	0.022	...	...	...	...
As	3×10^{16}	6.2	19.8 ± 0.4[b]	-53.4 ± 0.2[b,d]	-33.6[b]	10.0[f]
As[a]	4×10^{15}	1.5	...	...	...	...
Sb	6×10^{16}	26	9.1 ± 0.3[b]	-42.6[b,c]	-33.5[b]	8.3[f]
Bi	4×10^{16}	52	34 ± 2[b]	-70.6 ± 0.3[b,e]	-36[b]	...

[a] Mixed sample: 4×10^{15} donors/cc; 1.5×10^{15} P/cc; 2.5×10^{15} As/cc.

[b] Correction should be made for impurity banding for sample donor concentrations used for spin resonance and infrared absorption work. This correction will lower $E_{1S,\,D\&T}$ further.

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[f] These values have been determined from Wilson and Feher's values of Ξ_u/Δ and the Δ determined by spin-lattice relaxation (see reference 5).

ratio R_{As}/R_P shown in Table I for the dilute sample ($N_D \sim 4\times10^{15}$/cc). The intravalley orbit-lattice interaction alone would yield a ratio $R_{As}/R_P < 1$ because interference greatly reduces the interaction for $q_\Delta r \gg 1$.

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[13]Unlike the intravalley orbit-lattice interaction, the Umklapp intervalley orbit-lattice interaction also couples the 1S singlet to the 1S triplet states. Within experimental accuracy the data indicate no splitting of the doublet and triplet.

SPIRAL SPIN CONFIGURATIONS ACCOMPANYING EXCHANGE INVERSION

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We have recently observed in exchange inversion materials[1,2] of composition $Mn_{2-x}Cr_xSb$ with $x < 0.035$ that over certain temperature ranges a spiral (SP) spin configuration is stabilized as an intermediate state between the ferrimagnetic (F) and antiferromagnetic (AF) states. Transitions from F to SP and from SP to AF occur by first-order processes. These magnetic transitions occur without a detectable change in crystal symmetry. The symmetry change associated with the first-order transition takes place only in the spin system.

The discontinuous changes in c axis that establish each of these transitions as first order are shown in Fig. 1. Thermal hysteresis between cooling and warming curves is observed for transition temperatures below about 200°K; only the cooling curves are shown. The Kittel[3] relation, $\Delta c/M^2 = \text{constant}$, which has been found to apply[4] for $T_S > 200$°K, also applies to the double transition if the entire change in c from ferrimagnetic to antiferromagnetic states is used.

For samples with T_S less than ~100°K, the higher transition F/SP takes place on cooling as expected, but the lower transition SP/AF does not take place even on cooling to 4°K. The magnetization data of Fig. 2 illustrate this behavior. Curve 1 represents a specimen with $T_S > 200$°K for which no spiral state exists. Curve 2 ($T_S \approx 130$°K) shows the transition from ferrimagnetic to spiral to antiferromagnetic ordering. Curve 3 ($T_S \approx 90$°K) represents a specimen that remains in the spiral state.

The existence of a spiral spin configuration for the intermediate state has been established by neutron diffraction.[5] Ferrimagnetic layers containing equal numbers of Mn(I) and Mn(II) sites spiral about the c axis with a turn angle of 120°. The spiral is thus commensurate with the unit cell, the c axis of the magnetic unit cell being three times that of the chemical unit cell. The moments are perpendicular to c and have values of approximately 1.7 and 3.6 Bohr magnetons for Mn(I) and Mn(II), respectively.

Resistivity measurements furnish a simple method of following the transitions and differentiating the several magnetic states. As illustrated previously,[6] the high resistivity of Cr-modified Mn_2Sb arises almost entirely from electron-magnon scattering. As a result the resistivity associated with AF ordering is higher than for F ordering and has a different temperature dependence. We have found that the spiral state also has an associated resistivity which lies approximately half way between resistivities of the F and AF states. Such measurements have been