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Theory of spin-dependent effects in silicon

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Crystalline silicon with a large dislocation density shows a very complex magnetic-resonance spectrum. It is argued that this is due to exchange coupling between the "dangling-bond" electrons along the dislocation. A microscopic theory of this exchange as well as of the magnetic anisotropy is presented. The large spin-dependent recombination observed in dislocated silicon as well as amorphous silicon is shown to be associated with a multiphonon self-trapping process.

I. INTRODUCTION

Pure or lightly doped silicon, either n or p type, does not show a conventional EPR absorption. Lépine,[1] however, has shown that changes in photoconductivity provide a very sensitive method for observing the spin resonance of the recombination centers. By such a technique Lépine was able to observe spin-dependent recombination in crystalline silicon which he attributed to surface states.

If dislocations are now introduced into silicon by plastic deformation at high temperature, then both EPR[2] and photoconductivity[3] show bulk effects. This is not surprising, for every time a dislocation line crosses a row of atoms parallel to its Burgers vector we obtain an unpaired electron. Although this electron is often referred to as a "dangling bond," it is more likely a localized state derived from the conduction band.[4]

What is particularly interesting, however, is the fact that the EPR spectrum is very complex, containing what appear to be as many as 15 pairs of equally spaced lines symmetrically located on both sides of a central group of lines. The intensities of these pairs varies irregularly with distance from the center. Furthermore, these lines show an axial dependence when the applied magnetic field is rotated about the direction of the Burgers vector belonging to the great majority of dislocations, which in this case was [011]. Schmidt *et al.*[2] therefore suggested that the dangling-bond states each contain one electron and that these electrons couple ferromagnetically through an exchange interaction to form a total spin $s \gg \frac{1}{2}$. The observed spectrum is then that of a "superparamagnetic" moment in an axial crystal field. However, we estimate below that the exchange interaction between two lone-pair orbitals separated by 3.82 Å appears as *antiferromagnetic*. This would imply that the ground state of the dislocation is a Néel state with $S = 0$.

The photoconductivity also shows anomalous spin-dependent behavior. If $\Delta\sigma$ is the increase in the conductivity of the silicon due to the photoexcitation, then this excess conductivity is reduced by an amount $\delta(\Delta\sigma)/\Delta\sigma \simeq 60\times 10^{-6}$ at room temperature and 25×10^{-6} at 77 °K when the spin resonance of the recombination centers is saturated. If one assumes[1] that the recombination center consists of an electron and that the final state is a singlet, then the maximum effect expected based on the Pauli exclusion principle is $\delta(\Delta\sigma)/\Delta\sigma \simeq p_1 p_2$, where p_1 and p_2 are the polarizations of the combining spins. Under the experimental conditions this product has the value 10^{-6}. Lépine *et al.*[3] suggested that the anomalously large observed value is due to the formation of a magnetic polaron, although no detailed model was presented. In this note we suggest an alternative model that is consistent with both the EPR results and the photoconductivity measurements.

II. MAGNETIC HAMILTONIAN

A. Exchange

The first question we have attempted to answer is: What is the nature of the exchange interaction between the dangling bonds? To obtain some estimate of this we have calculated the separation between the lowest-lying singlet and triplet states associated with two dangling bonds. To carry out this calculation for two silicon atoms bonded to five other silicon atoms would be prohibitively difficult. We have, therefore, saturated the silicon bonds with hydrogen atoms placed at the silane (SiH_4) distance of 1.48 Å. The geometry of this Si_2H_6 molecule is shown in Fig. 1(a). A set of self-consistent orbitals was obtained using the GAUSSIAN 70 program of Hehre and Pople[5] with a self-consistent-field treatment of the ground state. The basis for this calculation consisted of 24 atomic states having Gaussian representations. We find that the dangling-bond orbital has the form

$$\phi = 0.40(3s) - 0.20(2p_z) + 0.58(3p_z) . \qquad (1)$$

The 34 electrons were then introduced and a configurational interaction calculation carried out to determine the excited states using the SPINCIP program of Gouyet and Prat.[6] The resulting spectrum is shown in Fig. 1(b). The singlet-triplet separation indicates an *antiferromagnetic* coupling of $2J = -6$ meV or 35 °K. This is, of course, a rough estimate. It does not, for example, allow for the possibility of indirect exchange through "backbridging" silicon atoms. Nevertheless, it is interesting to note that Broude *et al.*[7] have observed an anomaly in the magnetic susceptibility of dislocated silicon at 40 °K.

The excited state at 9.25 eV above the triplet corresponds to the configuration in which one of the dangling-bond electrons hops to the other to form a "lone pair." The large repulsive energy U is consistent with an antiferromagnetic Hubbard exchange $2J = -4t^2/U$, where the electron transfer integral t is much less than U, making a Heisenberg Hamiltonian a good approximation. We shall therefore assume that the low-lying states of the linear chain consist of a spin part multiplied by an orbital part Φ involving products of the dangling-bond orbitals (1). The spin part is obtained from the exchange interaction

$$\mathcal{H}_{\text{ex}} = 2|J| \sum_{j>i} \vec{s}_i \cdot \vec{s}_j \, . \tag{2}$$

The eigenstates for finite chains of spins with such coupling have been computed.[8]

B. Anisotropy

In Fig. 2(a) we show the structure of a dislocation in the diamond lattice. We see that the environment around the dislocation is "stretched" in the direction of the Burgers vector $\vec{b}$. This distortion produces a crystalline electric field which produces a magnetic anisotropy by distorting the excited orbitals. The interaction which couples the spins to their environment is the spin-orbit interaction. Let us introduce the coordinate system shown in Fig. 2(b) in which the z axis lies in the direction of the dangling bond and the x axis lies in the direction of the Burgers vector. For an orbital wave function of the form given in Eq. (1), $\langle \phi | l_\mu | \phi \rangle = 0$. Thus, we must consider second-order matrix elements involving an excited orbital state.

We expect the excited state to consist of a combination of $n = 4$ orbitals. Since these are more extended than the $n = 3$ orbitals they will be more sensitive to the anisotropic environment. We therefore assume an orbital of the form $\psi = a(4s) + b(4p_x)$. Furthermore, these orbitals will also have some overlap along the chain. This means that the orbital part of the excited eigenstates will involve a linear combination of the form

$$\psi_k = A \sum_i e^{ikR_i} c^{\dagger}_{i4} c_{i3} \Phi \, , \tag{3}$$

where the operator $c^{\dagger}_{i4} c_{i3}$ excites the electron at

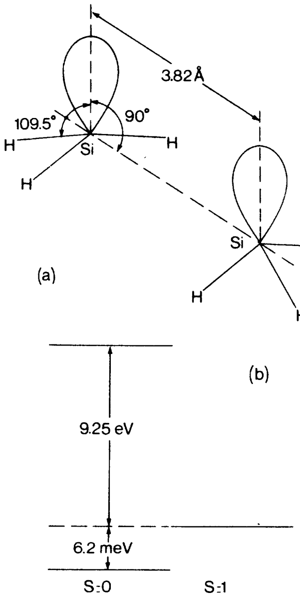

FIG. 1. (a) Geometry assumed in calculating the exchange between two dangling bonds. (b) Lowest-lying states of the Si_2H_6 molecule.

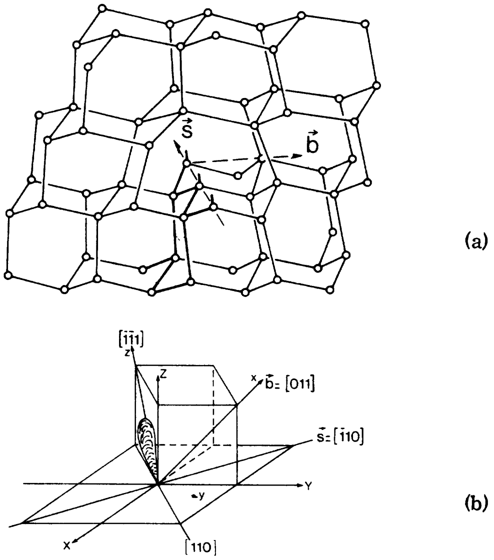

FIG. 2. (a) 60° dislocation in silicon. $\vec{s}$ indicates the direction of the dislocation and $\vec{b}$ the direction of the Burgers vector [after J. Hornstra, J. Phys. Chem. Solids 5, 129 (1958)]. (b) Coordinate system used in this calculation of the magnetic anisotropy.

site i from a $3sp$ orbital to the $4sp$, and A is a normalization factor which accounts for the nonorthogonality of these orbitals. This corresponds to a tightly bound, or Wannier, exciton, with an energy $E_k = E_1 - t^* \cos(n2\pi/N)$, where E_1 is the energy of the orbital ψ, and t^* is the transfer integral between excited orbitals on adjacent sites. The second-order corrections to the energy of a state $|S, M_s, \Phi\rangle$ involve matrix elements of the form

$$\langle S', M_s', \psi | \xi(r_i) l_i^\mu s_i^\mu | S, M_s, \Phi \rangle .$$

These may be factored into orbital and spin parts. Both are independent of the site i. Therefore, the sum over k leads to a Kronecker delta $N\Delta(k)$. Furthermore, writing

$$\langle S', M_s', | s_i^x | S M_s \rangle = \langle S', M_s' | S_x | S, M_s \rangle / N ,$$

the effect of the spin-orbit coupling may be described by the spin Hamiltonian

$$\mathcal{H}_{\text{anis}} = (0.58)^2 b^2 \frac{\lambda^2}{E_1 - E_0 - t^*} S_x^2 \equiv D S_x^2 . \qquad (4)$$

The integral of $\xi(r)$ between two $3p$ functions is of the order of tens of meV. Therefore, since the $3p$ and $4p$ orbitals are orthogonal we expect λ, which is the corresponding integral between the $3p$ and $4p$ orbitals, to be perhaps an order of magnitude smaller, say 5 meV. The energy E_1 between the $3sp$ state and the $4sp$ state is of the order of eV. If we take t^* to be 0.5 eV then $E_1 - E_0 - t^* \approx 0.5$ eV. With b of the order of 0.5 we estimate D to be 10^{-4} meV.

III. EPR SPECTRUM

Let us now apply an external magnetic field and calculate the magnetic-dipole spectrum we expect for this anisotropic chain. For simplicity, let the field be along the Burgers vector

$$\mathcal{H}_Z = -g \mu_B H S_x . \qquad (5)$$

A field of 3 kOe corresponds to 1 °K while $D \simeq 10^{-3}$ °K. Therefore, the anisotropy is a small perturbation on the Zeeman levels. The eigenvalues of $\mathcal{H}_Z + \mathcal{H}_{\text{anis}}$ within a given S multiplet are

$$E_{M_S} = -g \mu_B H M_S + D M_s^2 . \qquad (6)$$

The separation between multiplets depends upon the number of spins on the chain and their exchange coupling. If we neglect, for the moment, intermultiplet transitions, then we expect dipole transitions at

$$\hbar\omega = g\mu_B H + D(2M_S + 1) ,$$

$$M_S = -S, -S+1, \cdots, (S-1) . \qquad (7)$$

The relative intensities for $\Delta M_S = +1$ transitions will be proportional to $(S - M_S)(S - M_S + 1)$. Each multiplet in the spectrum will also contribute in proportion to its thermal excitation. In Fig. 3 we show the derivative of the absorption spectrum of the eight-spin chain for $T = 300$ °K. A Gaussian broadening with a width of $6D$ has been introduced. This is only approximate, of course, since in one dimension the line shape is neither Gaussian nor Lorentzian. We see that the spectrum has a complex shape reflecting the thermal distribution of the exchange levels of the chain. Note particularly that the zero of this derivative spectrum does not coincide with the center of the unweighted spectrum, making it difficult to assign a g value.

Chains with an odd number of spins will give complementary lines between those shown in Fig. 3. Chains with different numbers of spins will have different distributions of eigenstates. However, as long as each chain has the same anisotropy energy the positions of the lines will coincide, reinforcing their intensities. Longer chains will add more satellite lines to these shown for $N = 8$. We expect the spectrum to have the same qualitative features of that observed, although it is difficult to predict the intensity distribution for such longer chains.

The length of these antiferromagnetic segments is most likely limited by the appearance of doubly occupied sites. It has been suggested that such sites appear along the dislocation with some frequency of the order of one in ten giving the dislocation a negative core. The Coulomb re-

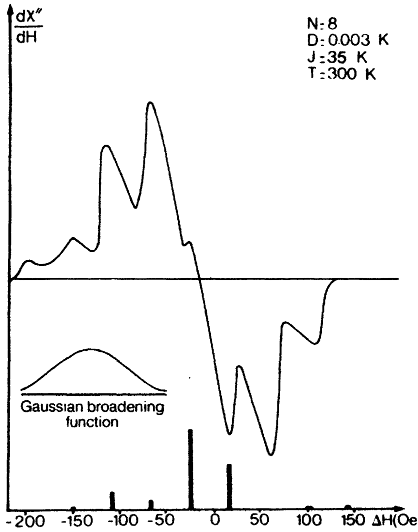

FIG. 3. Derivative of the absorption spectrum theoretically expected for a chain of eight spins ($S = \frac{1}{2}$) at $T = 300$ °K.

pulsion associated with such pairs is reduced by "reconstruction" of the surrounding lattice.

Now, what about the intermultiplet transitions? These may only occur if the multiplets differ by one spin reversal. Furthermore, in the EPR case only multiplets having the same wave vector will be coupled by the uniform microwave field. And, finally, the frequencies at which these transitions occur will differ for different length chains. Consequently their spectrum will be spread over a wide range making their presence undetectable.

IV. RECOMBINATION

As we mentioned in Sec. I, the photoconductivity of silicon samples containing a high density of dislocations shows an anomalously large spin dependence. The experimental arrangement is relatively simple: The sample is irradiated by microwaves, as in a standard resonance experiment, while simultaneously photoexciting carriers; the photoconductivity $\Delta\sigma$ is then measured as a function of the dc magnetic field. This photoconductivity shows a resonant behavior. By modulating the microwave power it is determined that the effect is due to a decrease in the recombination lifetime, not merely a decrease in the mobility of the carriers. In particular, when the modulation frequency exceeds the inverse recombination time, the resonance decreases.

Since the photoconductivity is three orders of magnitude smaller in dislocated silicon than in pure silicon it is obvious that the dislocations are playing a role in the recombination. The structure of a dislocation is very complex. It represents a region of very large strain in the crystal. Furthermore, the frequent appearance of lone pairs along the dislocation gives it a negative core, as we mentioned above. The screening of this charge produces a space charge around the dislocation which is believed to play an important role in recombination.[9] Our situation is further complicated by the high density of dislocations. At densities of the order of $10^8/\text{cm}^2$ the lattice is strongly disordered. Such disorder is known to produce a spectrum of localized states in the gap as occurs in an amorphous semiconductor. Lépine *et al.*[3] observe an optical absorption threshold at 0.7 eV in dislocated silicon compared with the indirect gap at 1.1 eV in pure silicon. Since the resistivity is p type with an activation energy of 0.46 eV, Lépine *et al.* suggest the transitions beginning at 0.7 eV are from states associated with the dislocations. Thus, we shall assume that the Fermi level of the dislocated silicon lies within this spectrum of localized states.

Since the photoconductivity is given by $\Delta\sigma = \Delta n e \mu$, and since the decrease in the photoconductivity has been experimentally associated with a decrease in the recombination time as opposed to a mobility effect, this implies that

$$\delta(\Delta\sigma)/\Delta\sigma = \delta(\Delta n)/\Delta n. \tag{8}$$

When carriers are optically excited a nonequilibrium steady state is established which is characterized by two Fermi levels, one for electrons and one for holes. If the number of photoexcited carriers is large compared with the number of centers, which we shall assume to be the case, these Fermi levels lie very close to the valence and conduction bands. Thus all the localized states become recombination centers and the number of photogenerated electrons may be written

$$\Delta n = f/N_0 v \Sigma , \tag{9}$$

where f is the generation rate of electrons and holes, N_0 is the density of centers, v is the thermal velocity of the electrons, and Σ is the cross section for capture by a localized state.

Lax[10] and Ascarelli and Rodriques[11] have calculated the cross section for electron capture by a Coulomb center. In this case, the cross section becomes larger as the binding energy becomes smaller. But the probability for thermal reemission also increases. Therefore the total cross section will reflect a balance between those two effects. This is described by writing the cross section as

$$\Sigma = \sum_n \Sigma_n P_n , \tag{10}$$

where Σ_n is the cross section for capture into a state at energy E_n below the conduction band, and P_n is the probability that the electron will continue down to the ground state before escaping. Using the principle of detailed balance Σ_n can be related to the probability *per unit time* β_n for thermal ionization of an electron in state n. The "sticking" probability P_n may then be written

$$\begin{aligned} P_n = 1 &- \beta_n \Big/ \Big(\beta_n + \sum_{m \neq n} w_{mn} \Big) \\ &- \sum_{m \neq n} \Big[\beta_m \Big/ \Big(\beta_m + \sum_{l \neq m} w_{lm} \Big) \Big] \\ &\times w_{mn} \Big/ \Big(\beta_n + \sum_{n \neq n} w_{mn} \Big) - \cdots , \end{aligned} \tag{11}$$

where w_{mn} is the probability *per unit time* that an electron in state n makes a transition to start m.

In order to apply this formalism we must have a knowledge of the recombination centers. Unfortunately, it has not been clearly established whether the resonance observed in the photoconductivity is, in fact, identical to that observed in the imaginary part of the magnetic susceptibility, $\chi''(\omega)$, i.e., the EPR. As we saw above, the EPR of dislocated silicon has a very complex structure, making it difficult to assign a g value. Although Wosinski *et al.*[12] have observed structure in the spin-dependent photoconductivity a detailed comparison with the EPR spectrum has not been made.

Since we have already argued that the dislocation behaves like an exchange-coupled linear chain, we considered the possibility that the carriers are captured by the dislocations in a spin-wave-assisted cascade process. This is analogous to the phonon-assisted cascade capture calculated by Lax[10] and Ascarelli and Rodriques.[11] The resulting cross section is proportional to the spin-spin correlation function $\langle S_q S_{-q}(\omega)\rangle$, where q is the change in momentum of the electron upon capture and $\hbar\omega$ its energy loss. There are several difficulties with this process, however. If $\hbar\omega_E < k_B T$, as we estimated, then we find that the spin-spin correlation function is not temperature-dependent enough for the microwave heating of the spins to produce much effect.[13] More significant, however, is the fact that an anomalously large spin-dependent recombination has also been observed in hydrogenated amorphous silicon prepared by *rf* plasma decomposition of silane[14] as well as in a silicon n^+-p junction.[15] The g values associated with the photoconductivity resonance in these three systems are all the same. This is an argument for a recombination center common to these different systems.

In the amorphous silicon there is only a very weak EPR absorption in the dark,[16] presumably due to the saturation of the dangling bonds by the hydrogen. The optically induced EPR in this case occurs at the same g value as the resonance in the photoconductivity. However, the power required to saturate the photoconductivity resonance is much larger than that required to saturate the EPR. This means that the "object" affecting the photoconductivity has a shorter T_1. Also, the light-induced spin density n_L, and $\delta(\Delta\sigma)/\Delta\sigma$ behave differently with doping.[14,16] And, finally, it is important to note that the photocurrent decays much faster than the EPR signal after the light is turned off. These results suggest that the photocarriers first decay into deep traps, generating the spin density measured by EPR.

One possibility we considered was that the electron and hole initially form a bound triplet exciton. If the triplet is in the $m_s = -1$ state its decay to the singlet state is spin forbidden, i.e., the sticking probability is very small. If the triplet were excited to its $m_s = 0$ state by magnetic resonance, however, then the transition becomes allowed and the sticking probability is increased. Such a process is well known in phosphorescent materials[17] where the radiative triplet-to-singlet transition is enhanced by EPR. Such a triplet is not involved here, for this process requires that the EPR signal decay with the same time constant as the photoconductivity which, as we mentioned above, is not the case.

Thus, if we are left with a number n_L of spins after the photocurrent has decayed, and since the number of spins in the dark is $n_D \ll n_L$, it appears that the photocarriers are being trapped by what is initially a spinless center. The simplest possibility is that the spin traps itself through a local atomic rearrangement. In this mechanism, we assume that the photocarriers drop into shallow states near E_v and E_c. From here the carrier may be reemitted to an extended state or drop into a deep localized state with the emission of N phonons. The role of the microwave resonance is to heat up the local environment thereby enhancing the phonon emission, i.e., increasing the sticking probability. This sequence is illustrated in Fig. 4.

The rate at which energy is absorbed by the spin is

$$\pi = (M_o - M_z)H/T_1\,, \tag{12}$$

where $M_o = \chi H = (\mu^2/k_B T)H$. At saturation, we have

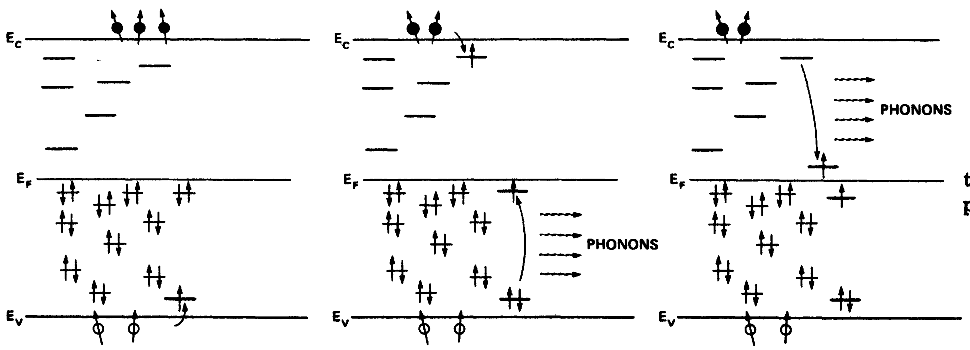

FIG. 4. Schematic illustration of the recombination process.

$M_z = 0$. We must now assume that the immediate environment around the spin may be considered as a thermodynamic system with its own temperature and heat capacity C. This might, for example, be the local system generally represented by a configurational coordinate diagram. If this system transfers its energy to the lattice beyond in a time τ^*, then in equilibrium at saturation the temperature rise δT of the local phonon system is obtained by equating the power in to the power out

$$\mu^2 H/k_B T T_1 = C\delta T/\tau^* . \tag{13}$$

Thus

$$\delta T/T = (\tau^*/T_1)(C/k_B)^{-1}(\mu H/k_B T)^2 . \tag{14}$$

The rate equations governing the number of carriers n and the occupation of shallow traps N is

$$\frac{dn}{dt} = f - \frac{n}{\tau_1} + \frac{N}{\tau_2} , \tag{15}$$

$$\frac{dN}{dt} = \frac{n}{\tau_1} - \frac{N}{\tau_2} - \frac{N}{\tau_3} . \tag{16}$$

Here f is the optical generation rate, τ_1 is the rate of capture by the shallow trap, τ_2 is the rate of reemission to the conduction band, and τ_3 is the rate associated with the multiphonon decay. In equilibrium

$$n = f\left[\left(\frac{1}{\tau_1}\right)\left(1 - \frac{1/\tau_2}{1/\tau_2 + 1/\tau_3}\right)\right]^{-1} . \tag{17}$$

We have written the result in this form to show that it has the structure required Eqs. (8), (10), and (11) with the second factor in the denominator representing the sticking probability. Thus

$$\frac{\delta(\Delta n)}{\Delta n} = -\frac{\Delta\Sigma}{\Sigma} = -\frac{\Delta P}{P} = \frac{\tau_3^2}{\tau_2 + \tau_3}\Delta\left(\frac{1}{\tau_3}\right) = \frac{\tau_3^2}{\tau_2 + \tau_3}\frac{\partial}{\partial T}\left(\frac{1}{\tau_3}\right)\delta T . \tag{18}$$

The relaxation rate $1/\tau_3$ for N-phonon emission is proportional to $[n(T)+1]^N$, where $n(T) = [\exp(\beta\hbar\omega_0) - 1]^{-1}$ and ω_0 is some characteristic phonon frequency.[18] If the deep state lies ΔE below (above) $E_c(E_v)$ then $N = \Delta E/\hbar\omega_0$. Thus we finally have the result

$$\frac{\delta(\Delta\sigma)}{\Delta\sigma} = \frac{\tau_3}{\tau_2 + \tau_3}\frac{\tau^*}{T_1}\frac{\Delta E}{k_B T}\frac{n(T)}{C/k_B}\left(\frac{\mu H}{k_B T}\right)^2 . \tag{19}$$

At room temperature $k_B T$ very likely exceeds the phonon energy $\hbar\omega_0$. Therefore, $n(T) \simeq k_B T/\hbar\omega_0$, and the heat capacity C/k_B is just the number atoms making up the "environment" N_0. Since τ_2 probably involves the absorption of one phonon we expect $\tau_2 < \tau_3$. As an estimate of τ^*, we take the recombination time τ itself. Thus

$$\frac{\delta(\Delta\sigma)}{\Delta\sigma} \sim \frac{\tau}{T_1}\frac{\Delta E}{\hbar\omega_0}\frac{1}{N_0}\left(\frac{\mu H}{k_B T}\right)^2 . \tag{20}$$

For a divacancy N_0 would be of the order of six. Taking Lépine's value[1] for τ/T_1 of 35 and $\Delta E/\hbar\omega_0 \sim 20$ we obtain an "enhancement factor" of 120. Thus, this self-trapping model is capable of explaining the large enhancement factors observed. Also, through the linear dependence on ΔE, it explains why $\delta(\Delta\sigma)/\Delta\sigma$ decreases[14] as the Fermi level moves toward either band. The condition $\tau^* > T_1$ corresponds to a phonon "bottleneck."

Also, since the photoconductivity resonance in this model is that of a shallow localized electron, it is more extended and therefore interacts more with other localized spins decreasing T_1 relative to that of the deeply trapped more-localized electron. The field dependence predicted by this model will depend upon the field dependence of T_1.

This discussion illustrates how useful the spin dependence of the photoconductivity can be in providing clues in identifying the recombination mechanism.

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