FIG. 1. Results of reference 1 plotted in terms of reduced variables.

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# Spin Resonance in $V$-Centers

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KÄNZIG[1] has recently observed spin resonances at $-180°C$ in KCl, NaCl, KBr, and LiF, all x-irradiated at $-180°C$. He attributes the resonance to that center responsible for the $V_1$-band[2]; the manner of defect production and the thermal bleaching of the
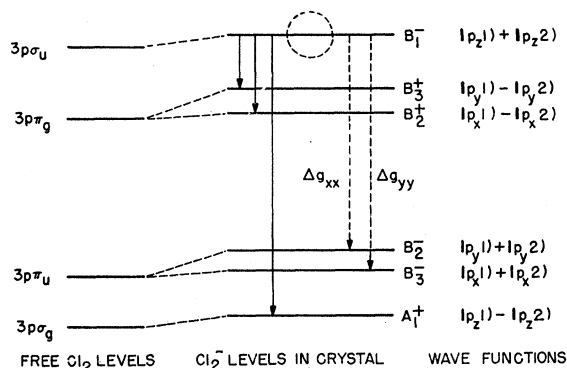


FIG. 1. Schematic representation of $V_3$-levels. The hole is in the $B_1^-$ level. Allowed optical transitions are indicated by solid arrows, mixing of levels giving rise to $\Delta g$ by dotted arrows. $z$ parallels the $Cl_2^-$ axis, [110], and $y$ the vacancy-pair axis, [1$\bar{1}$0]. $|p_z1\rangle$ represents the $p$-function of type $z$ centered on atom one, etc.

resonance support this view.[3] The spectrum coincided in detail with that expected from a hole localized on two halogen ions. For KCl, these "$Cl_2^-$ molecules" had cylindrical symmetry about axes parallel to $\langle 110 \rangle$, $\Delta g_{||}=0$, and $\Delta g_\perp=0.040$. Känzig has presented results in detail only for KCl; we restrict ourselves to KCl in the following.

Let the term $V$-center refer to the models listed by Seitz[2] and the term $V$-band refer to the optical absorption bands as labeled by Seitz.[2] We now discuss the spin resonance patterns to be expected from the $V_1$- and $V_3$-centers.

$V_1$-*center.*—The observed localization of the hole suggests a tight-binding approximation. Group theoretical considerations yield explicitly the possible wave functions of electrons in the $3p$-shells of Cl ions neighboring the vacancy. No wave function so obtained is consistent with localization of the hole on less than four Cl atoms. Very crude guesses as to the relative energies of the levels indicate that a 3-fold level might lie highest. If so, the $V_1$-center would have a very short relaxation time, for the Jahn-Teller splitting of the level should be small in such crystals.

On the other hand, if one accepts localization on two atoms, one is hard put to get cylindrical symmetry about a [110] axis. We suggest that the observed spectrum was not that of the $V_1$-center. The latter might be observable at He temperatures.

$V_3$-*center.*—We assume the hole to be entirely localized on the two common nearest neighbors of the vacancy pair. The $V_3$-center has orthorhombic symmetry, $D_{2h}$. A group theoretical analysis yields wave functions and selection rules for optical transitions and for the $g$-shift. Wave functions, energy levels, and their relations to those of the $Cl_2^-$ molecule are indicated schematically in Fig. 1. For a hole in the $B_1^-$ level, $\Delta g_{||}=0$. For $\Delta g_{xx}$ approximately to equal $\Delta g_{yy}$ requires a small $B_2^-$, $B_3^-$ energy separation. A small splitting of the $3p\pi_u$ levels requires in turn a considerable decrease in the $Cl-Cl$ spacing.

It thus seems likely that the $V_3$-center, and not the $V_1$-center, is the source of Känzig's resonance. It also seems likely that the $V_3$-center is still to be associated with the $V_3$-band, etc., as proposed by Seitz.[2] For if we take the atomic spin-orbit parameter, $\lambda$, as 587 cm$^{-1}$, $\Delta g_\perp$ as 0.040, and 70% for the $p$-character of the wave function[1] [admixture of $s$-character into $B_1^-$ can arise from $|s1\rangle - |s2\rangle$], we obtain 41 000 cm$^{-1}$ for the energy separation of $B_1^-$ and $B_2^-$ or $B_3^-$. This value is reasonable relative to the value 47 200 cm$^{-1}$ for the optical transition $B_1^-$ to $A_1^+$ obtained by associating the $V_3$-band with the $V_3$-center. Further, *some* $V_3$-absorption *is* produced by x-irradiation at $-180°C$.[2,3] When holes are released by thermal dissociation of the $V_1$-centers present in larger numbers, they are trapped by the negatively charged $V_3$'s, turning the latter into diamagnetic $V_2$-centers.[2,3] This process can therefore explain the observed bleaching behavior.

If the line width, $\Delta\nu$, arises entirely from hyperfine-structure relaxation, it should be proportional to the sum of the squares of the two nuclear $g$-factors. We find $(g_1^2+g_2^2)/\Delta\nu$ equal to 0.25, 0.255, and 0.26 for $Cl^{35}-Cl^{35}$, $Cl^{35}-Cl^{37}$, and $Cl^{37}-Cl^{37}$, respectively. This constancy indicates little spin-spin interaction for KCl and confirms the extreme localization of the hole.

The observed localization and $g$-factors imply considerable lattice distortion. Such distortion can be understood in terms of the above level scheme. The empty level rises as the Cl—Cl separation decreases; the five occupied levels should have a net lowering of energy. Stability of isolated $V_3$-centers with respect to thermal dissociation might well be a consequence of the distortion.

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[2] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).
[3] D. Dutton and R. Maurer, Phys. Rev. **90**, 126 (1953).

# Relaxation Effects in Recombination Velocity on Germanium Surfaces under Transverse Electrostatic Fields

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THE surface recombination velocity ($s$) of a given chemically treated germanium surface can be changed by the application of transverse electrostatic fields, as described by Henisch and Reynolds.[1] By employing this technique, relaxation phenomena in $s$ were observed here which were not reported by those authors.[2] These effects are similar in character to the relaxation phenomena encountered in surface conductivity (field effect)[3-6] and in channel conductance in $n$-$p$-$n$ junctions.[6,7]

The experimental procedure was as follows. A rectangular filament (0.2–0.6 mm thick), etched in $CP4$,[8] was placed between two interconnected metal plates and isolated from them by thin (0.02 mm) mica spacers. Voltages (up to 1500 volts) were applied between the metal plates and the filament. The quantity $s$ was computed[9] from filament lifetime measurements employing the bridge method.[10] The relaxation effects were investigated by field cycles consisting of (1) application of positive field (i.e., plates positive), (2) field off, (3) application of negative field of equal intensity, and (4) field off. In each stage, the variation of $s$ with time was followed. Repeated successive cycles showed good reproducibility. The relaxation times observed in various filaments ranged from few minutes to several hours. Typical cycles are shown in Figs. 1 and 2. The measurements were carried out in vacuum. The same types of curves were obtained when the mica spacers were removed.
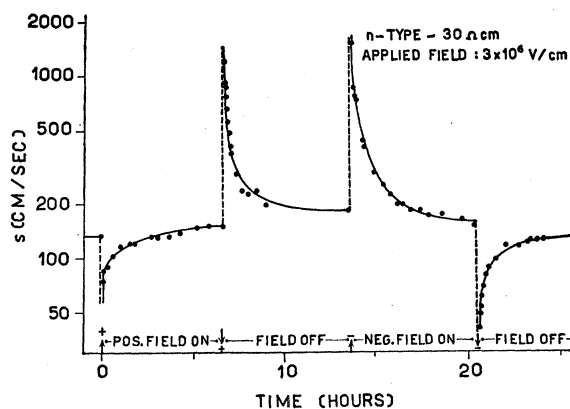


Fig. 1. A field cycle of surface recombination velocity, typical for long relaxation times.

The relaxation in channel conductance and surface conductivity (field effect) has been attributed[6,7] to the transfer of electrons between states on the germanium-germanium oxide interface and states on the outer surface of the oxide film. The same mechanism is found to explain satisfactorily the relaxation in $s$ observed here. On the application of the field, say positive, electrons are drawn to the germanium-germanium oxide interface and a new equilibrium is set up between the barrier layer and the states at the interface, such that practically all field lines terminate at the interface. This process, which probably extends over a time of several tens of microseconds (of the order of filament lifetime),[4] results in a rapid depression of barrier height and hence[11] effects a corresponding change in $s$. As, however, the electrons move from the interface to the outer surface of the oxide (under the action of the field), they gradually screen the interface from the external field. As a result, $s$ relaxes towards its initial equilibrium value. The relaxation time is determined by the characteristics of the potential barrier in the oxide film.[7] This barrier hinders the electronic transfer and could explain the long time constants observed. When the field is switched off, the excess
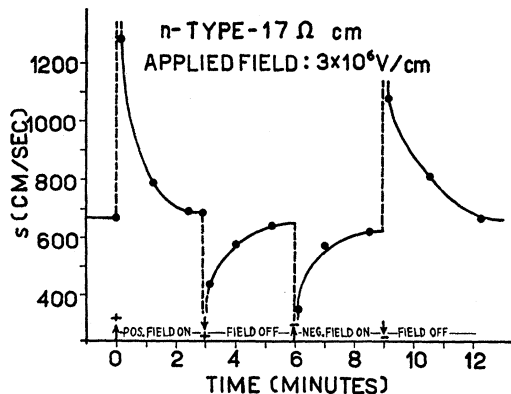


Fig. 2. A field cycle of surface recombination velocity, typical for short relaxation times.