# High-resolution spectroscopy of silver-doped silicon

J. Olajos, M. Kleverman, and H. G. Grimmeiss
*Department of Solid State Physics, University of Lund, Box 118, S-221 00 Lund, Sweden*
(Received 6 July 1988)

Silver-doped silicon was investigated by using transmission and photothermal ionization spectroscopy (PTIS). A spectrum of sharp lines was detected between 6200 and 6700 $cm^{-1}$. In PTIS, strong phonon-assisted Fano resonances were observed which involved $f$ TO and $g$ LO intervalley phonons. It was therefore possible to identify the silver-related center as a donor. The Ag spectrum differs from previously reported donor spectra in silicon in the sense that excitations to excited $p$ states do not dominate. $2p_0$ and $3p_0$ lines were weakly observed, and none of the usually strong $p_\pm$ lines were detected. By comparing spectra of P and neutral Te with the spectrum obtained for Ag, it is shown that the Ag spectrum is dominated by excitations to $s$ states.

## I. INTRODUCTION

Deliberate doping of silicon with silver gives rise to several deep centers.[1] Investigations of the electrical properties of some of these centers have shown that the two most commonly observed levels have binding energies of about $E_a = E_v + 0.54$ eV (4355 $cm^{-1}$) and $E_d = E_v + 0.34$ eV (2742 $cm^{-1}$) (Ref. 1). They are denoted Ag($A$) and Ag($D$), respectively, since one of them [Ag($A$)] is assumed to be an acceptor, whereas the other is believed to be a donor.

The potential experienced by a charge carrier bound to a neutral deep center consists of two parts. One part is given by the central-cell potential which has short-range character and is caused by local effects due to, for example, differences in the bonds between the impurity and its neighbors compared with the bonds of the perfect crystal. The other part is the long-range screened Coulomb potential which is responsible for the appearance of shallow excited states. High-resolution spectroscopic studies in silicon have recently revealed detailed information on excited Coulomb states of both deep donor[2,3] and acceptor[4–6] centers which are well described by the effective-mass approximation (EMA). It could be shown that the localized central-cell potential causes only minor changes in the binding energies of $p$ states with respect to their EMA values, whereas $s$ states are significantly affected, resulting in considerable energy shifts. In EMA, only excitations from the $1s$ ground state to excited $p$-like states are electric-dipole allowed (Fig. 1). This is the reason why optical spectra observed for neutral chalcogen donors in silicon are very similar to those obtained for shallow donors, although they are observed at much higher photon energies due to the larger binding energies of the ground states.

All shallow donor states in silicon are at least sixfold degenerate because of the six equivalent conduction-band minima. This degeneracy is partly lifted by the valley-orbit interaction which mostly affects the $s$ states since it is only these that have a nonvanishing amplitude at the impurity site. In $T_d$ (tetrahedral) symmetry, all $ns$ states split into a singlet $ns(A_1)$ state, a doublet $ns(E)$ state, and a triplet $ns(T_2)$ state, where $A_1$, $E$, and $T_2$ are irreducible representations of the $T_d$ point group. For centers with lower symmetry than $T_d$ the residual degeneracies of the $ns$ multiplets may be further reduced in accordance with the relevant point-group symmetry. Most of the donors in silicon have a $1s(A_1)$ ground state which is the only state in the $1s$ multiplet that has a nonvanishing amplitude at the impurity site. Exceptions to this rule are the thermal donors[7] which have one of the $1s(T_2)$ components as the ground state and the interstitial Li donor[8] which has a $1s(E+T_2)$ ground state. In Fig. 1, a survey is given of the EMA and symmetry-allowed electric-dipole transitions from the $1s(A_1)$ ground state to excited states of a shallow donor with $T_d$ symmetry. These transitions have been observed not only for shallow but also for deep donors such as the chalcogen double donors in silicon. It is, however, important to notice that the EMA selection rules weaken if the ground state of the center is no longer well described by EMA as, for example, demonstrated by an increasing binding energy, resulting in a considerable increase in the intensity for those lines which are caused by transitions to $ns$ states. An interesting example for such behavior is given by the EMA-forbidden but symmetry-allowed $1s(A_1)$-$1s(T_2)$ transition of chalcogens in silicon which has an intensity comparable to that of the $1s(A_1)$-$2p_0$ line which is otherwise one of the most intense lines for shallow donors. There is good reason to expect that for donors still deeper than the chalcogens the strength of the $ns$ lines may exceed the strength of other lines and thus dominate the optical spectrum due to an increasing localization of the wave function of the donor ground state.

Acceptor states have been observed in silicon with binding energies still larger than those for donors. Two of these acceptors which have been studied in great detail are the gold and platinum acceptors.[4–6] In both cases very sharp line spectra have been observed. Considering that only excitations to excited $p$-like states are observed, it is interesting to note that their overall features are very similar to those obtained for the group-III shallow acceptors. These data suggest that for moderately deep donors

 

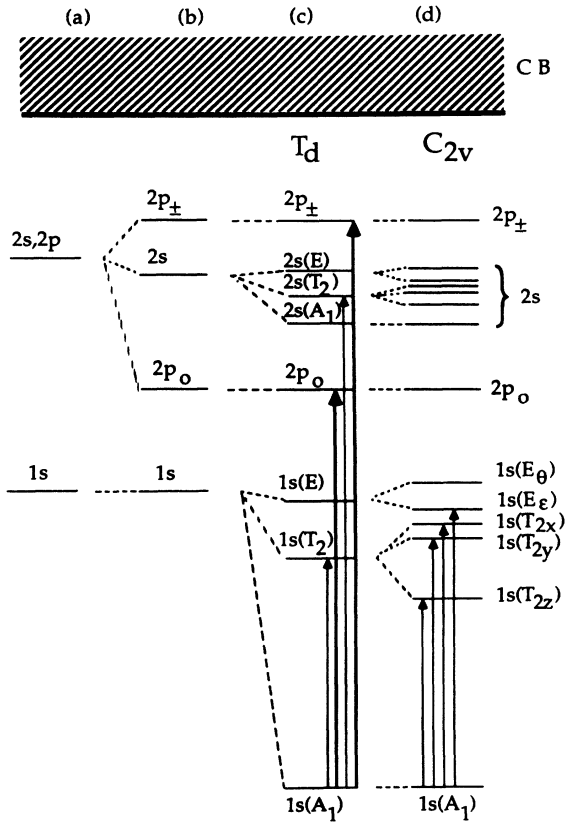


FIG. 1. Schematic figure showing the energy positions of *ns* and *np* states (for different approximations and point-group symmetries) for donors in silicon. The EMA and symmetry-allowed transitions are indicated by heavy arrows and transitions only symmetry-allowed by fine arrows. (a) Isotropic effective mass. (b) Anisotropic effective mass. (c) Valley-orbit interaction included for a center with $T_d$ symmetry. (d) Valley-orbit interaction included for a center with $C_{2V}$ symmetry (only transitions to 1*s* states are indicated).

and very deep acceptors the *p* states, compared with the *s* states, are obviously relatively insensitive to the central-cell potential.

Silver as well as gold and copper belong to group 1*B* of the Periodic Table. The free silver atom has one 5*s* electron outside the filled 4*d* shell, while gold has one 6*s* electron outside the filled 5*d* shell. It is, therefore, not unreasonable to assume that single substitutional Ag and Au centers in silicon should have similar electrical and optical properties. This assumption seems to be confirmed considering that the binding energy of the Au acceptor is about $E_a = E_v + 0.63$ eV and that of the donor $E_d = E_v + 0.35$ eV (Ref. 9). Such a comparison is only useful if it is assumed that the silver and gold centers have similar microscopic structures. However, no data have yet been published revealing the lattice position of the silver centers. It is also not known whether the Ag(*A*) and Ag(*D*) levels really belong to the same center, i.e., whether or not they are due to transitions from a neutral center to different charge states of the same defect. Furthermore, there is no support yet for the presumed acceptorlike and donorlike behavior of Ag(*A*) and Ag(*D*) in the literature.

In this paper we report for the first time on the observation of sharp line spectra in Ag-doped silicon which have been studied using photothermal-ionization spectroscopy[10] (PTIS) and Fourier–transform infrared (FTIR) transmission spectroscopy. It will be shown that the Ag spectra differ from previously studied donor and acceptor spectra in silicon in the sense that the Ag-related line spectra are not dominated by transitions from the ground state to *p*-like Coulomb states. By comparing the Ag spectra with spectra obtained in tellurium-doped silicon evidence is given that the strongest lines are caused by transitions from the very deep ground state to excited *s* states. Phonon-assisted Fano resonances[11,12] are observed in PTIS which strongly support our suggestion that the Ag center studied in this paper is a donor. Since the binding energy of this center is close to the one previously reported for the Ag(*D*) donor we have good reason to believe that the center investigated by us is the Ag(*D*) donor. Several phonon replicas of transitions from the ground state to other excited 1*s* states involving pseudolocalized phonons are observed and discussed.

## II. EXPERIMENTAL DETAILS

Silver was diffused into samples originating from 14-Ω cm *p*-type and 200-Ω cm *n*-type floating-zone silicon. The samples were lapped, polished, and etched in $HF + H_2O$, prior to evaporation of an approximately 300-nm-thick silver layer. The samples were then introduced into quartz ampoules which were then evacuated, sealed, and heat treated at various temperatures between 600 and 1250 °C for various diffusion times between 1 and 340 h. After diffusion, the surface layers were lapped and polished again and, in the case of PTIS samples, provided with good Ohmic contacts by rubbing Ga-Al onto parts of the surface. All spectra were obtained with a Bomem DA 3.01 Fourier-transform spectrometer. The sample temperature was kept at about 10 K in a Leybold continuous-flow cryostat using liquid helium as coolant. To improve the transparency of the transmission spectra, an artificial background was produced. The original spectra were then divided by this background which resulted in a flat background of the processed spectra.

## III. RESULTS

Figure 2 shows a typical transmission spectrum of our Ag-doped silicon samples. Several sharp line structures are observed in the energy range 6200–6700 $cm^{-1}$ which have the same relative intensities in different samples. It is therefore believed that the lines originate from the same center. A further series of lines is seen at somewhat higher energies. Since the relative intensity of this series varied from sample to sample compared with the series at 6200–6700 $cm^{-1}$ it is very likely that the two spectra originate from different centers and the series at higher energies will therefore not be discussed in this paper.

The line spectrum presented in Fig. 2 shows no direct resemblance to previously studied line spectra observed

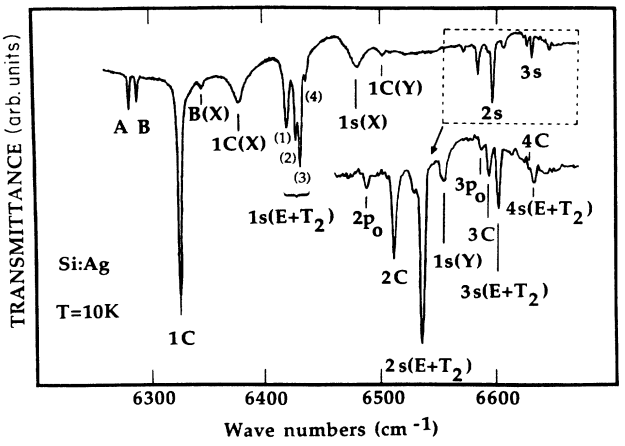


FIG. 2. Transmission spectrum of Ag-doped silicon. For the assignment of the lines see text.

for donors or acceptors in silicon, and it is therefore difficult to decide whether the spectrum is caused by an acceptor or a donor. Furthermore, none of the lines has an energy which is close to the activation energies previously reported for the Ag($A$) and Ag($D$) levels. On the other hand, the reported energy difference between the conduction band and the Ag($D$) level is about 0.83 eV (6694 $cm^{-1}$). This energy is close to the high-energy limit of the spectrum (Fig. 2) in general, and of the series of lines between about 6575 and 6650 $cm^{-1}$ in particular. It is therefore probable that the spectrum observed in our silver-doped samples is caused by the Ag($D$) center and that the lines observed are due to excitation from the ground state to localized excited Coulomb states just below the conduction band.

Further evidence that the spectrum presented in Fig. 2 is caused by a donor, namely the Ag($D$) center, was obtained by comparing the Ag spectrum with the spectra obtained for neutral chalcogen donors in general, and tellurium in particular (Fig. 3). In the case of the deep chalcogen donors, the $1s(E)$ and $1s(T_2)$ states have binding energies which are close to the $1s$ EMA value. When subtracting the $1s$ EMA value of 252 $cm^{-1}$ (Ref. 2) from the preliminary binding energy of the Ag($D$) center (6694 $cm^{-1}$), an energy of about 6442 $cm^{-1}$ is obtained. Considering this value as a rough estimate for the energy position of the $1s(E)$ and $1s(T_2)$ states of the Ag($D$) center it is interesting to note that close to this energy at about 6430 $cm^{-1}$ in Fig. 3 a sharp line structure is observed. We therefore tentatively assign this structure as originating from $1s(A_1)$-$1s(E+T_2)$ transitions of the Ag($D$) center, assuming the ground state to be $1s(A_1)$. The $1s(E+T_2)$ structure observed consists of four closely spaced lines indicating a lower symmetry than $T_d$ for the Ag($D$) center [Fig. 1(d)] since in $T_d$ symmetry only one line is expected, as only transitions from $1s(A_1)$ to $1s(T_2)$ are symmetry allowed [Fig. 1(c)].

Recent photoluminescence studies[13–15] of Au-doped silicon revealed a sharp line structure which was attributed to the $1s(E+T_2)$-$1s(A_1)$ transition of the Au donor. This assignment was confirmed by Zeeman and uniaxial stress measurements. Corresponding transitions have been observed in transmission. In Fig. 4 the Ag $1s(E+T_2)$ lines are compared with the corresponding lines of the Au donor. A remarkable similarity is observed which gives further support for our assignment of the structure at about 6430 $cm^{-1}$ as lines due to $1s(A_1)$-$1s(E+T_2)$ transitions of the silver donor.

Further information on the Ag spectrum was obtained from PTIS measurements. A typical PTIS spectrum is presented in Fig. 5. A comparison with the transmission spectrum of Fig. 2 shows that the two spectra are indeed caused by the same center. The bound-to-bound transitions and, at higher photon energies, the onset of the excitation to the conduction band (continuum part of the spectrum) are clearly seen. It is noteworthy that transitions which ionize the center directly give a positive contribution to the photocurrent (continuum part) whereas bound-to-bound transitions cause dips at lower energies in the spectrum, i.e., below the continuum part. These dips originate from the fact that a charge carrier which is excited from the ground state to an excited state does not contribute to the conductivity unless it is thermally excit-

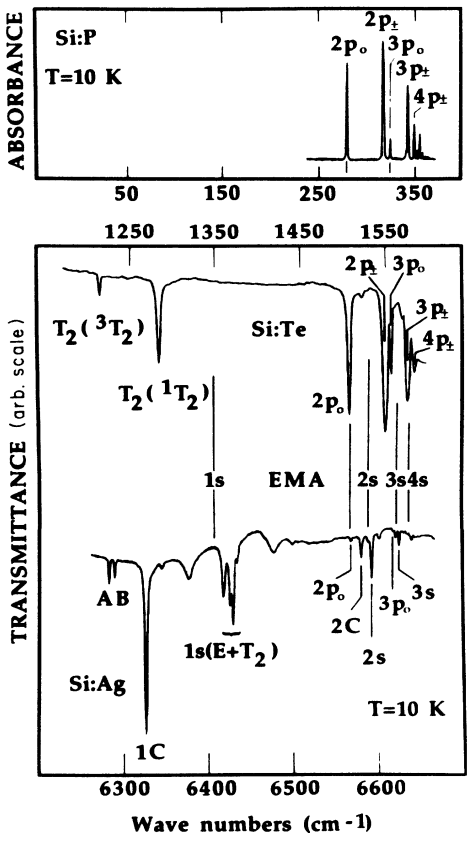


FIG. 3. Comparison between the Ag spectrum and the spectra obtained for the P donor and the neutral Te donor. The energy scales are chosen such that positions of the $2p_0$ lines coincide. The EMA values for different $ns$ states are obtained from theory.

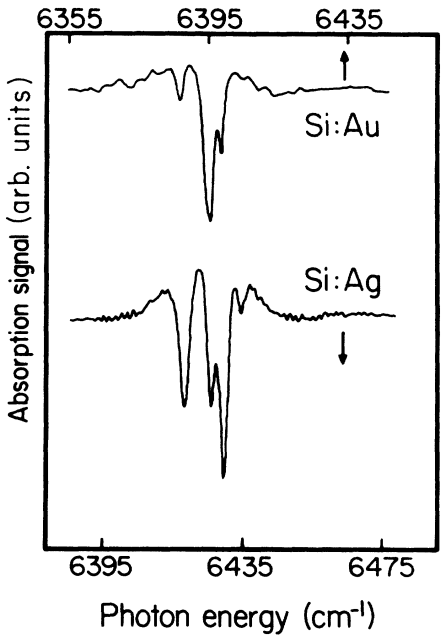


FIG. 4. Comparison of the $1s(A_1)$-$1s(E+T_2)$ lines for the Ag and Au donor.

ed into the continuum. Lines due to shallow excited states are therefore favored in PTIS, compared with deeper excited states. The total conductivity signal is a superposition of contributions from several different excitation processes and centers. The sharp line spectrum due to silver is therefore observed superimposed on a slowly varying background signal of much higher intensity caused by other defects. Intensities of lines observed in absorption or PTIS can therefore not be compared in a straightforward manner, since in PTIS the intensity of a

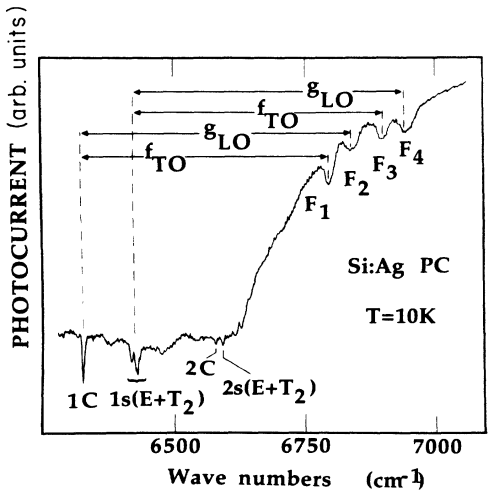


FIG. 5. PTIS spectrum of the Ag donor showing excitation lines due to bound-to-bound transitions and direct excitations to the electronic continuum as well as phonon-assisted Fano resonances. The phonons involved in the resonances are indicated.

superimposed spectrum is measured in relation to all other spectra obtained in the sample simultaneously. The signal in PTIS due to a particular excitation process depends on the efficiency for the generation of free charge carriers of this particular process compared with all other generation processes. The bound-to-bound transitions at lower energies are therefore observed in Fig. 5 as dips, since such transitions absorb photons and contribute less to the photoconductivity compared with other more-efficient excitation processes at these photon energies. The positive peaks at higher energies are caused by bound-to-bound transitions involving excited states with smaller binding energies and, hence, larger thermal emission rates than those at lower energies.

The PTIS signal of the Ag($D$) center was very weak and consequently only a few of the most intense lines could clearly be resolved. Nevertheless, some very important information could be obtained from these measurements. The threshold energy for the onset of transitions from the ground state directly into the conduction band is easily deduced (Fig. 5) to be about 0.82 eV (6620 $cm^{-1}$). This result further supports our assignment of the spectrum, namely that it is caused by the Ag($D$) center. The data also confirm that the lines close to the onset of the continuum part in Fig. 5 are most probably caused by excited Coulomb states.

An additional interesting spectral feature was observed in the continuum part of the PTIS spectrum of Fig. 5 which we identify as phonon-assisted Fano resonances. Optical excitations from the ground state of a center to the electronic continuum can, under certain circumstances, be resonant with excitations from the ground state into an excited state, if a bulk phonon is emitted simultaneously. This process has been discussed in terms of phonon-assisted Fano resonances and has been observed for several shallow and deep centers in silicon. Although, in principle, three different intervalley phonons[12] are allowed for donors, namely the $f$ LA (387.9 $cm^{-1}$), $g$ LO (515.4 $cm^{-1}$), and $f$ TO (476.6 $cm^{-1}$), it has been shown experimentally that only the $g$ LO and $f$ TO phonons couple strongly enough to be observed in phonon-assisted Fano resonances. Since in the case of acceptors only the zone-center $\Gamma$ phonon (519 $cm^{-1}$) has been found to couple, a study of Fano resonances offers the unique possibility of identifying the type of center, i.e., whether it is an acceptor or a donor. The FWHM of the phonon-assisted Fano resonances observed for the silver donor in PTIS (Fig. 5) is about 20 $cm^{-1}$. It is therefore difficult to decide whether a $g$ LO or a $\Gamma$ phonon is involved because of the similarity of the two phonon energies. If, however, an $f$ TO phonon is shown to participate in a Fano-resonance process it is highly probable that the center is a donor. Experimentally it is found that an $f$ TO resonance is in most cases accompanied by a $g$ LO phonon resonance. It is therefore possible to identify the type of the silver center, not only from the line spectrum of excited states but also from the appearance of Fano resonances involving the $f$ TO phonon.

Fano resonances are, in general, more clearly observed in PTIS than in absorption, thus we prefer to study them in PTIS. Four major resonances, denoted $F_1$-$F_4$ are

TABLE I. Phonon-assisted Fano resonances for the Ag donor lines. The mean values of the $1s(E+T_2)$ lines is used for the energy of $1s$ in the table.

| Transition | Transition energy ($cm^{-1}$) | Interpretation | Electronic plus phonon energy ($cm^{-1}$) |
|---|---|---|---|
| $F_1$ | 6800 | $1C+f$ TO | 6803 |
| $F_2$ | 6845 | $1C+g$ LO | 6842 |
| $F_3$ | 6902 | $1s+f$ TO | 6904 |
| $F_4$ | 6949 | $1s+g$ LO | 6943 |

clearly seen in Fig. 5. The photon energies involved are summarized in Table I. A closer inspection of the resonances (Fig. 5) and of the corresponding energies (Table I) reveals that both the relative intensities and energy differences of the resonances appear in pairs. The energy difference between the pairs $F_1$-$F_2$ and $F_3$-$F_4$ is about 104 $cm^{-1}$ which is close to the energy difference of 98 $cm^{-1}$ for the two dominating PTIS line structures which we consider as a strong argument for the assignment of the continuum structure as Fano resonances. The energy difference between the partners in each pair is about 45 $cm^{-1}$. This value is somewhat larger than the energy difference between the $g$ LO and $f$ LO intervalley phonons, which is only 38 $cm^{-1}$. The difference in energy is nevertheless rather small, which can easily be seen by shifting the dominant PTIS lines by a $g$ LO and $f$ TO phonon energy, respectively, to higher energies as indicated by arrows in Fig. 5. The resulting energies are in fair agreement with the observed resonances giving further support for our assignment.

An intervalley phonon participates in the scattering of an electron from one conduction-band valley to another. In EMA, the wave function of a bound state is built up from continuum states close to the bottom of the conduction band (donors) or the top of the valence band (acceptors). The involvement of an $f$ TO phonon in the phonon-assisted Fano resonances of the Ag center is therefore in agreement with the assignment of the Ag($D$) center as a donor.

## IV. DISCUSSION

Both the PTIS and the transmission data presented so far suggest that the Ag-related line spectrum is due to excitation from a deep donor ground state to shallow excited states. As discussed above, all sharp line spectra of previously observed shallow and deep donors in silicon are dominated by lines originating from excitations to $p$ states. This is seen in Fig. 3, where the spectra of the neutral phosphorus and tellurium donors in silicon are replotted by shifting the energy scales such that the positions of the $2p_0$ lines coincide. The Ag spectrum also shown in Fig. 3 seems to be very different compared with the two other spectra. At first glance, it is therefore difficult to find a common feature which could be used as a guide for the shift of the energy scale in order to facilitate a comparison with the other two spectra. If lines within the $1s$ multiplet are excluded, the $2p_0$ line is known to be the one with the lowest energy for all donors in silicon. Although it cannot be excluded, it is nevertheless rather unlikely that the binding energy of any of the allowed $2s$ states should be increased by a strong central-cell potential to such a degree that it becomes larger than the binding energy of the $2p_0$ state. When analyzing the Ag spectrum it was therefore assumed that the lowest line above the $1s$ multiplet is caused by the $2p_0$ state. Assuming that the $2p_0$ state shows only a minor central-cell correction, the binding energy of the Ag($D$) center is calculated to be 826 meV (6661.2 $cm^{-1}$) by adding the theoretical EMA binding energy of $2p_0$ (92.68 $cm^{-1}$) to the measured transition energy (6568.53 $cm^{-1}$). Excluding the $1s$ multiplet, the $2p_0$ line of a donor spectrum in silicon is normally the one with the largest binding energy, while the $2p_\pm$ lines has the highest intensity. No $2p_\pm$ line has been observed in the Ag spectrum. Shifting the energy scales of the spectra in Fig. 3 such that the $2p_0$ lines coincide, it is seen that the relative intensity of the $p$ lines in the Ag spectrum is very weak compared with the other two spectra.

The energy position of different $ns$ states can be estimated from their EMA values which are indicated in Fig. 3. The energy position of the $1s$ EMA state is seen just below the previously discussed $1s(E+T_2)$ multiplet and the EMA positions of additional $s$ lines are close to other groups in the Ag spectrum. It is reasonable to presume that each group of lines is caused by corresponding transitions from the assumed $1s(A_1)$ ground state to split $ns$ states. We therefore denote these lines the $ns(E+T_2)$ lines.

A closer inspection of the tellurium spectrum (Fig. 3) shows that there is a weak line just below the $1s(T_2)$ line which has been previously proven to be the spin-triplet state of the $1s(T_2)$ state. Neutral tellurium binds two electrons and via exchange interaction one spin-singlet and one spin-triplet series are formed.[16] The ground state of the single substitutional tellurium donor is a singlet, and electrical dipole transitions from the ground state to the triplet series are therefore, in principle, forbidden. In the case of tellurium, however, a strong spin-orbit interaction mixes the $T_2$ levels originating from the singlet $T_2$ [$T_2(^1T_2)$] and triplet $T_2$ [$T_2(^3T_2)$] states so that both the singlet and triplet $T_2$ levels become visible. Comparing the tellurium spectrum with the silver spectrum (Fig. 3) and assuming that there exists an exchange interaction between the loosely bound electron and the electrons of the donor core, it is tempting to suggest that the $A$, $B$, and $1C$ lines may originate from similar many-particle and spin-orbit effects.

Each $ns(E+T_2)$ line is accompanied by another line at somewhat lower energy (Fig. 2) which we believe is the corresponding $C$ line for various $n$. In the limit of a strong localization of the electrons in the defect core the exchange splitting, for example, is proportional to the probability of finding the delocalized excited electron at the impurity site. This probability is given by $|\Psi_n(0)|^2$ where $\Psi_n(0)$ is the value of the wave function of the excited electron at the origin. For hydrogenic $ns$ states,

$\Psi_n(0) \sim 1/n^{3/2}$ and, hence, the splitting is expected to scale approximately as $1:\frac{1}{8}:\frac{1}{27}$ for $n=1$, 2, and 3. In the case of the deep Ag donor, the exchange interaction between an electron in the delocalized $1s(T_2)$ state and the strongly bound electron(s) is expected to follow roughly the same scaling. As already mentioned, the energy difference between the two dominating line structures of the Ag spectrum, i.e., the $C$ line and the $1s(E+T_2)$ multiplet, is about 100 $cm^{-1}$. If it is assumed that both structures involve $1s$ states due to exchange splitting, then the corresponding splitting of the $2s$, $3s$, and $4s$ states should be about 13, 4, and 2 $cm^{-1}$, respectively. This is indeed observed, as is readily seen from Fig. 2 where the energy differences between the $ns(E+T_2)$ and $nC$ lines are found to be about 12, 4, and 2 $cm^{-1}$ for $n=2$, 3, and 4, respectively. To show this interesting agreement in more detail we have plotted the different $ns$ multiplet in Fig. 6 using energy scales which are scaled in accordance with the $ns$ splitting, i.e., $1:\frac{1}{8}:\frac{1}{27}:\frac{1}{64}$.

A linear clearly resolved but not yet assigned is seen in Fig. 2, about 49 $cm^{-1}$ above the $2p_0$ line. Considering that the corresponding EMA value is 48.5 $cm^{-1}$ we have good reason to believe that the line is caused by the $3p_0$ state (Table II).

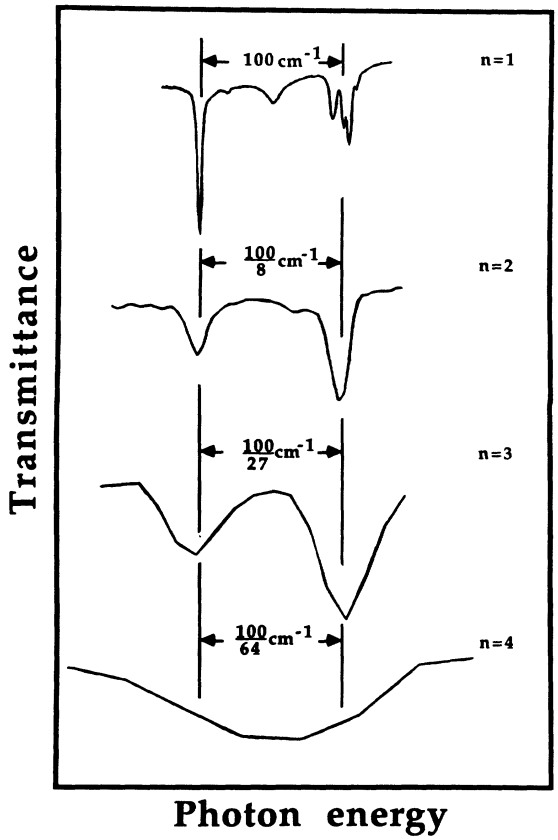


FIG. 6. Splitting of various $s$ states. The energy scales are multiplied by 1, 8, 27, and 64 for $n=1$, 2, 3, and 4, respectively, in order to demonstrate the scaling procedure discussed in the text.

TABLE II. Observed transition energies of the Ag-related donor lines in Si and corresponding calculated binding energies. For comparison the corresponding EMA values are also shown.

| Assignment | Photon energy ($cm^{-1}$) | Binding energy ($cm^{-1}$) | EMA ($cm^{-1}$) |
|---|---|---|---|
| $A$ | 6282.3 | 380.3 | |
| $B$ | 6289.9 | 372.7 | |
| $1C$ | 6326.2 | 336.4 | 252.13 |
| $1s(E+T_2)$ (1) | 6418.5 | 244.1 | 252.13 |
| $1s(E+T_2)$ (2) | 6426.1 | 236.5 | 252.13 |
| $1s(E+T_2)$ (3) | 6429.6 | 233.0 | 252.13 |
| $1s(E+T_2)$ (4) | 6434.4 | 228.2 | 252.13 |
| $2p_0$ | 6569.9 | 92.7 | 92.68 |
| $2C$ | 6582.0 | 80.6 | 71.42 |
| $2s(E+T_2)$ | 6594.2 | 68.4 | 71.42 |
| $1s(Y)$ | 6602.3 | 60.3 | |
| $3p_0$ | 6619.0 | 43.6 | 44.24 |
| $3C$ | 6622.3 | 40.3 | 38.53 |
| $3s(E+T_2)$ | 6626.2 | 36.4 | 38.53 |
| $4s(E+T_2)$ | 6641.0 | 21.6 | 23.48 |

Phonon replicas of excited Coulomb states in silicon have only rarely been observed. One example, which has recently been studied in detail, is the substitutional Pt center showing that several phonon replicas can occur. Since two broad structures are seen in the Ag spectrum of Fig. 2, roughly the same energy distance (50 $cm^{-1}$) above the $1C$ line [$1C(X)$] and the $1s(E+T_2)$ multiplet [$1s(X)$], these two lines may be considered as phonon replicas. Similar replica are observed about 50 $cm^{-1}$ above the $B$ line [$B(X)$ in Fig. 2]. The FWHM of the $1s(X)$ replica is somewhat larger than the FWHM of the $1C(X)$ replica and probably contains several $1s(E+T_2)$ lines.

At somewhat higher energies than the $1s(X)$ replica, another line is seen [$1C(Y)$] which we have so far been unable to assign in our analysis. The energy distance of this line from the $1C$ line is about 180 $cm^{-1}$. At a similar distance of 180 $cm^{-1}$ above the $1s(E+T_2)$ lines a further line was observed [$1s(Y)$] which has not yet been assigned. Since the energy distance of these two lines from the $1C$ line and the $1s(E+T_2)$ lines, respectively, is very similar we suggest that these lines should also be considered as phonon replicas.

The 50-$cm^{-1}$ ($X$) and 180-$cm^{-1}$ ($Y$) phonons are resonant with the silicon acoustic phonons and are therefore best discussed in terms of pseudolocalized phonons. The FWHM is larger for the $X$ than for the $Y$ replicas which may indicate that the $X$ phonon interacts more strongly with the band phonons than the $Y$ phonon.

The $A$ and $B$ lines were not observed as phonon-assisted Fano resonances and one may wonder whether they indeed originate from the Ag($D$) center. However, since they were always observed with the same relative intensity compared with all other lines in all our samples we consider it quite probable that they are caused by the silver donor. This interpretation is supported by the fact that both lines seem to have phonon replicas involving the same $X$ phonon as the $1C$ line and $1s(E+T_2)$ replicas.

To the best of our knowledge, the Ag($D$) spectra seem to be the first donor spectra observed in silicon which are not dominated by transitions to $p$ states. Moreover, the $2p_{\pm}$ line, normally observed as the strongest line for other donors with excited Coulomb states, is not observed at all. These particular properties of the silver spectrum may result from the very large binding energy of the silver donor, which is almost equal to the band gap. Excluding $1s$ states, the electronic structure of shallow or moderately deep donors, such as the chalcogens, is well described by EMA. In EMA the wave function of a donor is obtained as the product of the envelope function and the Bloch waves close to the conduction-band minima. With increasing strength of the central-cell potential the binding energy of the $1s(A_1)$ ground state increases, but simultaneously the probability for previously EMA forbidden transitions may increase. A consequence of the increased binding energy and, hence, degree of localization in real space is that a larger part of the conduction-band minima in **k** space contributes to the wave function of the $1s(A_1)$ ground state. Simultaneously the overlap between the wave functions of the ground state and excited Coulomb states decreases and so do the electric dipole matrix elements. Since no-phonon lines are observed as direct transitions in **k** space, this means that the relative intensity of the lines due to transitions to excited Coulomb states decreases. This effect is strongest for $p$ states since $s$ states are more affected by the central-cell potential than $p$ states and therefore are more delocalized in **k** space. One would therefore expect that for a donor with increasing deviation from EMA the relative intensity of transitions to $s$ states becomes so strong, compared with transitions to $p$ states, that they dominate the excitation spectrum.

Though this explains the prevailing properties of $s$ states we still have to explain why $np_0$ states are observed but not $np_{\pm}$ states. This is done by recalling that the effective mass is anisotropic in silicon and that the constant-energy surfaces are ellipsoids along equivalent $\langle 100 \rangle$ directions. The principal components of the effective-mass tensor are the longitudinal ($m_l$) and transverse ($m_t$) effective masses. Since $m_l > m_t$, the curvature of the conduction band is smaller along the $\langle 100 \rangle$ direction than in the perpendicular directions. A $p_0$ state is oriented in the $\langle 100 \rangle$ direction as in $m_l$ whereas a $p_{\pm}$ state is oriented along the $m_t$ principal axis. This implies that it is easier for a $p_0$ state to localize in real space than for a $p_{\pm}$ state since more energy is needed for a $p_{\pm}$ state to include more Bloch waves into the wave function.[17] For the same reason as above, the electric-dipole matrix elements of $p_0$ states for a very deep donor are then expected to be larger than those of $p_{\pm}$ states, which means that excitations to $p_0$ states are still seen when excitations to $p_{\pm}$ states are already too weak to be observed.

Figure 2 shows that the $1s(E+T_2)$ multiplet consists of four well-resolved lines [(1)–(4)], three of which [(1), (2), and (3)] have comparable intensities while the fourth line [(4)] has a much smaller intensity. In $T_d$ symmetry and negligible spin-orbit coupling, excitations from the $1s(A_1)$ ground state are only allowed to the three degenerate $1s(T_2)$ states [Fig. 1(c)]. Assuming that the Ag spectrum (Fig. 2) is due to one-electron transitions our data strongly suggest that the symmetry of the Ag($D$) center is lower than $T_d$ since four lines are observed. Four lines can therefore only originate from a $C_{2V}$ or lower symmetry, as supported by preliminary uniaxial stress experiments. In $C_{2V}$ symmetry the $T_2$ state splits into three components and the $E$ state into two [Fig. 1(d)]. Symmetry considerations show that excitations to all $T_2$ components are possible whereas excitations to only one of the $E$ states are allowed. Moreover, excitations to $E$ states are weak as long as the deviation from $T_d$ symmetry is small. A possible explanation of why four lines are observed for the $1s(E+T_2)$ multiplet is therefore that three are due to the $T_2$ state while the fourth originates from the $E$ states. These results are consistent with the so-called vacancy model[18] proposed, for example, for the neutral substitutional Ag center in silicon. In this model the silver atom is trapped in a vacancy and the $5s$ electron occupies a vacancy orbital. Through successive Jahn-Teller distortions the symmetry of the substitutional lattice position is lowered to $C_{2V}$ symmetry.

## V. CONCLUSIONS

Excitation spectra of the Ag($D$) donor in silicon due to transitions from the deep ground state to Coulomb excited states have been investigated. The donor character of the center is demonstrated by studying phonon-assisted Fano resonances involving the intervalley $f$ TO phonon. The assignment of the spectra relies on the assumption that the overlap between the ground state and excited $p$ states is small in **k** space, while it is considerably larger for $s$ states, in contrast to moderately deep donors such as chalcogens. Consequently, the spectra are dominated by lines due to transitions between the ground state and split excited $s$ states. Absorption measurements suggest that the symmetry of the Ag($D$) center is $C_{2V}$ or lower.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge discussions with B. Bech Nielsen and G. Grossmann and are indebted to L. Timby and E.-L. Hellqvist for help with sample preparation. We would also like to thank the Swedish Natural Science Research Council and the Swedish Board for Technical Development for financial support.

[1]N. Baber, H. G. Grimmeiss, M. Kleverman, P. Omling, and N. Zafar, J. Appl. Phys. **62**, 2855 (1987), and references therein.

[2]E. Janzén, R. Stedman, G. Grossmann, and H. G. Grimmeiss, Phys. Rev. B **29**, 1907 (1984).

[3]P. Wagner, C. Holm, E. Sirtl, R. Oeder, and W. Zulehner, in *Festkörperprobleme*, edited by Grosse (Vieweg, Braunschweig, 1984), Vol. 24.

[4]G. Armelles, J. Barrau, M. Brousseu, B. Pajot, and C. Naud,

Solid State Commun. **56**, 303 (1985).
[5]M. Kleverman, J. Olajos, and H. G Grimmeiss, Phys. Rev. B **35**, 4093 (1987).
[6]M. Kleverman, J. Olajos, and H. G. Grimmeiss, Phys. Rev. B **37**, 2613 (1988).
[7]M. Stavola, K. M. Lee, J. C. Nabity, P. E. Freeland, and L. C. Kimerling, Phys. Rev. Lett. **54**, 2639 (1985).
[8]A. K. Ramdas and S. Rodriguez, Rep. Prog. Phys. **44**, 1297 (1987).
[9]S. Braun and H. G. Grimmeis, J. Appl. Phys. **45**, 2658 (1974).
[10]Sh. M. Kogan and T. M. Lifshits, Phys. Status Solidi (A) **39**, 11 (1977).
[11]G. D. Watkins and W. B. Fowler, Phys. Rev. B **16**, 4524 (1977).
[12]E. Janzén, G. Grossmann, R. Stedman, and H. G. Grimmeiss, Phys. Rev. B **31**, 8000 (1985).
[13]J. Mazzaschi, J. C. Brabant, B. Brousseau, J. Barrau, M. Brousseau, and F. Voillot, Solid State Commun. **39**, 1091 (1981).
[14]D. Thebault, J. Barrau, M. Brousseau, Do Xua Thanh, J. C. Brabant, F. Voillot, and Mme. Ribault, Solid State Commun. **45** (1983).
[15]D. Thebault, J. Barrau, G. Armelles, N. Lauret, and J. P. Noguier, Phys. Status Solidi B **125**, 357 (1984).
[16]K. Bergman, G. Grossmann, H. G. Grimmeiss, and M. Stavola, Phys. Rev. Lett. **56**, 2827 (1986).
[17]G. Grossmann (private communication).
[18]G. D. Watkins, Physica B + C **117&118B**, 9 (1983).