Interstitial magnesium acts as a moderately deep double donor in silicon, and is relatively easily introduced by diffusion. Unlike the case of the chalcogen double donors, the binding energies of the even-parity valley-orbit-exciton states 1sT and 1sE have remained elusive. Here we report on temperature dependence absorption measurements focusing on the neutral charge species. Our results demonstrate thermal activation from the ground state 1sA to the valley-orbit states, as observed by transitions from the thermally populated levels to the odd-parity states 2p0 and 2p±.

Interstitial magnesium (Mg) in silicon is a deep double donor defect that has been the subject of several past investigations, which have uncovered many features of the neutral (Mg0) and singly ionized (Mg+) species. Recent investigations have provided more detail and revealed new complexity, including information about complexes Mg forms with other defects. Mg incorporates into Si primarily as an interstitial defect, and inhabits the tetrahedral (T4) interstitial site. Relative to many single and double donor impurities in Si, such as the Group-V shallow single donors and Group-VI deep donors, the moderately deep double donor Mg center has not been studied as comprehensively. While transitions to its odd parity excited states have been studied in some detail, there have been relatively few investigations of the even parity excited states. A thorough understanding of the electronic structure of Mg may prove important in the design of semiconductor lasers using intracenter electronic transitions. Transitions to even parity excited states in particular are important to a complete understanding of cascade relaxation processes. In such processes, electrons are initially captured by highly excited states and slowly diffuse to the impurity ground state through the ladder of available energy levels. Phonon(s) are emitted at each step of the ladder.

A proposal by Morse et al. has recently suggested the use of deep donor centres in silicon (Si) as the basis for a new spin qubit-photonic cavity technology. The proposed technology relies on transitions from the ground state to the valley orbit level 1sT2 which are forbidden within the effective mass theory (EMT) approximation. These transitions can be very strong for exceptionally deep donors such as the chalcogen donors, however no sign of these levels has been seen in absorption for Mg in Si until very recently. Mg is a double donor intermediate in depth between the shallow donors of Group-V and the deep-double donors of Group-VI. It may therefore lack the exceptionally strong central cell potential that allows for EMT-forbidden optical transitions between 1sA and 1sT2. Electronic dipole transitions between 1sA and 1sE are in addition forbidden by parity, though potentially visible in Raman scattering. However, previous experiments have not revealed the presence of such transitions in Raman spectra of Si:Mg samples.

Electronic transitions involving valley orbit excited states have been studied in past investigations of shallow donors like P, As, Sb, and Bi. By thermally populating the 1sE and 1sT2 states the authors were able to observe transitions to higher hydrogenic states such as 2p0 and 2p±. This technique is of course not viable for studies of very deep donors, and Pavlov et al. suggest that, as the shallowest of the deep donors, Mg0 may be close to the limit of its viability.

Preliminary results discussed by Pavlov et al. have suggested binding energies of 47.4(1) meV and 49.9(2) meV for the 1sE and 1sT2 levels of Mg0, respectively, by observing weak transitions between these levels and 2p±. An additional estimate by Pavlov et al. was calculated from the absorption spectra of Si:Mg samples subjected to a uniaxial strain. These measurements suggested a binding energy for 1sT2 of 49.8(1) meV in the unstrained sample. Previous work by Ho and Ramdas established an empirical estimate of the 1sA to 1sE transition energy for Si:Mg of 56.24 meV based on piezospectroscopic measurements. Binding energies determined in this work and by Pavlov et al. are somewhat lower than this value. Exceptionally deep donors, e.g. S, Se, Te, are known to have even smaller 1sE binding energies of ~31 meV meaning their 1s valley-orbit states are more hydrogen-like than helium-like. As the shallowest known isolated double donor, Mg is thought to be more helium-like than the deeper double donor impurities. As such, its somewhat deeper binding energies of the 1sT2 and 1sE valley orbit excited states relative to S, Se, and Te, closer to the estimate of Ho and Ramdas, is not unexpected. In this study we elaborate on the work of Pavlov et al. demonstrating that the valley-orbit states 1sT2 and 1sE of Mg0 may indeed be thermally populated, leading to clearly resolved transitions from both valley-orbit states to the odd-parity states 2p0 and 2p±.

In this study we measure the absorption spectra of a float-zone grown Si sample diffused with Mg. Parameters for Si:Mg sample preparation have been discussed in detail by Shuman et al. Here we work with a lightly compen-
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A saturated Si sample with a boron concentration of approximately $1 \times 10^{13} \text{ cm}^{-3}$, corresponding to the $\text{nat}$ Si low boron (LB) sample studied in our previous work.

This sample was not selected for maximum $\text{Mg}^0$ concentration, as was done in the preliminary study but rather for the highest ratio of the desired $\text{Mg}^0$ absorption as compared to other absorption transitions in the 30 to 45 meV region. Many weak transitions in this region are as-yet unidentified, and can obscure the relatively weak transitions of interest.

All absorption measurements were performed using a Bruker IFS 125HR Fourier transform infrared (FTIR) spectrometer. A coated Mylar beam-splitter was used, along with a 4.2 K silicon bolometer with an 800 cm$^{-1}$ low-pass cold filter. Samples were mounted on a temperature-regulated stage inside a liquid helium cryostat with polypropylene windows.

In Fig. 1 we see thermally-induced absorbance resulting from transitions between the valley-orbit excited states and the higher-lying odd parity states $2p_0$ and $2p_\pm$. Some processing was necessary to remove an Si phonon feature corresponding to $\text{TO}_1-\text{TA}_1$. This was noted experimentally at 39.04 meV and predicted theoretically by Franta et al. at 38.79 meV. Removal of this feature was accomplished by subtracting the appropriate absorbance spectra, which were taken using ultrahigh purity (UHP) undoped Si at each temperature seen in Fig. 1.

The integrated intensities of curve fits to the peaks in Fig. 1 are displayed as a function of inverse temperature in the Arrhenius plots shown in Fig. 2 normalized at each temperature by the area of the $2p_0$ transition. These Arrhenius curves correspond to the strongest pair of peaks seen in Fig. 1, namely transitions from $1sT_2$ and $1sE$ to $2p_\pm$. From the slopes of these we extract activation energies of 62.3 meV and 65.2 meV for the $1sT_2$ and $1sE$ transitions to $2p_\pm$ respectively. We note that these are both slightly higher than the optical spacings, which place $1sT_2$ and $1sE$ at 57.64 meV and 60.30 meV respectively above the ground state $1sA$. This small disagreement likely results from our inability to measure the sample temperature directly for temperature above 4.2 K. The observed optical spacings indicate binding energies of 47.20(1) meV and 49.86(1) meV for $1sE$ and $1sT_2$ respectively, in excellent agreement with the preliminary results of Pavlov et al.

We note that there were no signs of similar thermal activation of the valley-orbit excited states for the singly ionized species $\text{Mg}_i^+$. This was not unexpected, since the energy differences between $1sA$ and $1sT_2/1sE$ for the singly ionized species is considerably larger than for $\text{Mg}^0$. Given the 256.49 meV binding energy of the $\text{Mg}_i^+$ ground state, EMT calculations of valley orbit excited state binding energies for double donors by Altarelli suggest spacings of 101.49 meV (256.49 meV) between $1sA$ and $1sT_2/1sE$ for $\text{Mg}_i^+$.

Expanding upon the results of Pavlov et al. we have demonstrated clear evidence of thermal activation to the valley-orbit levels $1sT_2$ and $1sE$, leading to transitions to both the $2p_0$ and $2p_\pm$ excited states of $\text{Mg}^0$. Within a small constant offset, the activation energies extracted from Arrhenius plots associated with the $1sT_2$ and $1sE$ to $2p_\pm$ transitions are noted to agree well with the observed optical spacings. No
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signs of similar transitions from the 1sT2 and 1sE valley orbit excited states of Mg+ i could be observed.

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