Mg-pair isoelectronic bound exciton identified by its isotopic fingerprint in ^{28}Si

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We use the greatly improved optical linewidths provided by highly enriched ^{28}Si to study a photoluminescence line near 1017 meV previously observed in the luminescence spectrum of natural Si diffused with Mg and suggested to result from the recombination of an isoelectronic bound exciton localized at a Mg-pair center. In ^{28}Si, this no-phonon line is found to consist of five components whose relative intensities closely match the relative abundances of Mg pairs formed by random combinations of the three stable isotopes of Mg, thus confirming the Mg-pair hypothesis. We further present the results of temperature-dependence studies of this center that reveal unusual and as-yet unexplained behavior.

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I. INTRODUCTION

Deep double donors in silicon have recently been proposed as the basis for a scalable qubit-photonic cavity technology [1]. Our recent reinvestigation [2] of the Lyman absorption transitions of deep double donor interstitial magnesium (Mg_i) in silicon clarified a number of issues raised in earlier studies [3–8] of mid-infrared absorption in Si diffused with Mg. The dominant interstitial location of Mg, acting as a double donor, is unusual, with other group-II elements such as zinc and beryllium forming primarily substitutional double acceptors in Si [9–11]. There is also evidence that magnesium may occupy a substitutional site in Si and act as a deep double acceptor (Mg_s), with deep-level transient spectroscopy on Mg-diffused samples showing hole emission attributed to Mg_s [12].

The dual character of magnesium as a substitutional double acceptor and an interstitial double donor implies the potential for formation of an isoelectronic bound exciton (IBE) center comprised of an Mg_i-Mg_s pair, similar to the well-known 1077 meV Be-pair IBE [13]. IBE centers are able to localize excitons much more tightly than shallow donors or acceptors and, thanks to their lack of nonradiative Auger decay, can provide very bright luminescence even when present at low concentrations. The availability of highly isotopically enriched ^{28}Si, together with its greatly reduced optical linewidths due to the near elimination of inhomogeneous broadening [14], makes possible a new method of determining the chemical constituents of an IBE binding center. This method, known as isotopic fingerprinting [15,16], is an extension of the well-known method of no-phonon (NP) line isotope shifts [17]. The narrow linewidths in ^{28}Si result in distinct spectral components for all possible combinations of the stable isotopes comprising the IBE binding center, instead of just the shift of a relatively broad line which is seen in natural Si.

The photoluminescence (PL) results presented in this work follow the results of Steinman and Grimmeiss [18], who proposed that a Mg_i-Mg_s IBE pair center might be responsible for a NP line observed in the PL at 1017 meV. Here we confirm this hypothesis through high-resolution PL spectroscopy of ^{28}Si diffused with natural Mg. The 1017 meV NP line is revealed to consist of five distinct peaks with relative intensities matching those anticipated for a center containing two Mg atoms given the abundances [19] of the three stable naturally occurring Mg isotopes: 78.951(12)% ^{24}Mg, 10.020(8)% ^{25}Mg, and 11.029(10)% ^{26}Mg. Temperature-dependence measurements of the PL of this IBE center revealed unusual behavior of the main NP line and associated local vibrational mode (LVM) and phonon replicas.

II. MATERIALS AND METHODS

The sample studied here was examined in our previous [2] study of absorption transitions in Mg-doped Si, where it was referred to as ^{28}Si low boron (LB). Shuman *et al.* [20,21] detailed the methods used for the diffusion of Mg into Si. The starting material was enriched to 99.995% ^{28}Si and has been thoroughly described elsewhere [22]. All PL measurements were performed by using a Bruker IFS 125HR Fourier transform infrared (FTIR) spectrometer with a CaF_2 beam splitter. Samples were mounted loosely so as to avoid strain and cooled in a liquid helium cryostat. PL was generated by using 1030 and 1047 nm excitation sources for high resolution scans of the IBE and temperature-dependent PL measurements, respectively. Scattered excitation light was removed by sharp-cut long-pass filters. For PL measurements at

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temperatures above 4.2 K, the sample was lightly held against a temperature-controlled Cu plate cooled in flowing He gas. The PL was detected with a liquid-nitrogen-cooled Ge PIN diode detector. For the high-resolution isotopic fingerprint PL scans, an apodized instrumental resolution of 3.1 μeV full width at half maximum (FWHM) was used, while a lower resolution of 124 μeV FWHM was used for the temperature-dependence study, since for these studies lower excitation levels were necessary to minimize sample heating when the sample was not immersed in liquid He.

III. RESULTS

A. Isoelectronic bound exciton fine structure

In the PL spectrum of the Mg-doped ^{28}Si LB sample we observed a relatively strong NP feature at 1017 meV, which we label Mg_{NP}. This had been observed previously by Steinman and Grimmeiss [18] who suggested it might arise from a substitutional-interstitial Mg pair, in analogy with the well-known Be-pair IBE luminescence center [13]. Thanks to the near-elimination of inhomogeneous broadening made possible with ^{28}Si, the NP line is seen to resolve into five components, as shown in Fig. 1. The fit to the fine structure seen in Fig. 1 consists of five mixed Gaussian–Lorentzian peaks with an asymmetry parameter [23] that is kept constant for all peaks. This slight asymmetric broadening to low energy may be a consequence of Stark broadening due to random electric fields present even when using relatively lightly compensated starting material, due to Mg incorporating as both a substitutional (acceptor) and interstitial (donor) impurity.

The relative intensities of the five observed components closely match the expected relative abundances of Mg-Mg pairs with total masses ranging from 48 to 52 amu, as shown in Table I. The fact that the observed spectrum can be explained by grouping together isotope combinations having the same total mass indicates that the Mg atoms are indistinguishable from each other in terms of the NP isotope shifts, which is quite a common occurrence for other IBE centers in ^{28}Si whose isotopic fingerprints have been studied [16]. This result provides very strong confirmation for the proposal that the 1017 meV NP line observed in Mg-doped Si arises from a center containing a pair of Mg atoms.

TABLE I. Observed and predicted relative integrated intensities for peaks corresponding to Mg-Mg pairs. Total amu ranges from 48 to 52 depending on the combination of isotopes with ^{24}Mg-^{24}Mg comprising the largest fraction and ^{26}Mg-^{26}Mg the smallest. Absolute values of peak position are deemed accurate to two decimal places. Relative positions of the peaks to one another are considered valid to three decimal places.

	Integrated intensity		
$\sum$ Mg (amu)	Observed	Predicted	Peak energy (meV)
48	0.62(3)	0.62333(13)	1017.494
49	0.17(1)	0.15821(9)	1017.505
50	0.18(1)	0.18419(11)	1017.516
51	0.020(3)	0.02210(2)	1017.527
52	0.009(2)	0.01216(2)	1017.537

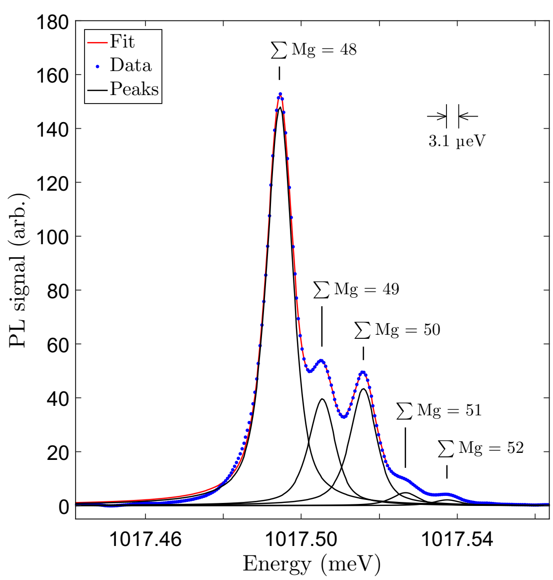

FIG. 1. Isotopic fingerprint of the magnesium isoelectronic pair center. The mass of the Mg-pair center in amu corresponding to each possible combination of naturally occurring isotopes is labeled. Spectra were collected at a resolution of 3.1 μeV with 1031 nm laser excitation.

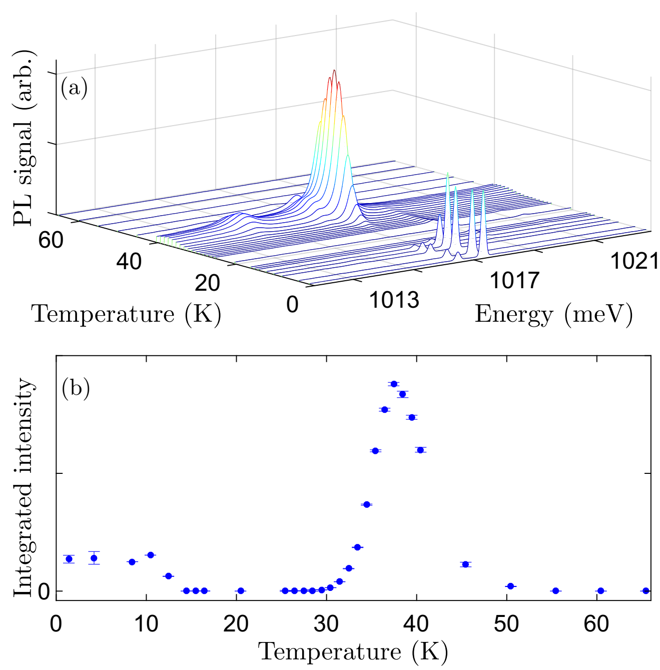

FIG. 2. (a) Waterfall plot showing the temperature dependence of the Mg-Mg IBE line and replicas. Up to ∼10 K the IBE features are relatively unchanged, but then decrease rapidly with increasing temperature until they disappear completely above ∼17 K. A resurgence of the IBE PL with increased linewidth and intensity along with a new LVM phonon replica become visible above ∼30 K. Spectra were collected at a resolution of 124 μeV with 1047 nm laser excitation. (b) Integrated intensity of the Mg_{NP} line as a function of temperature.

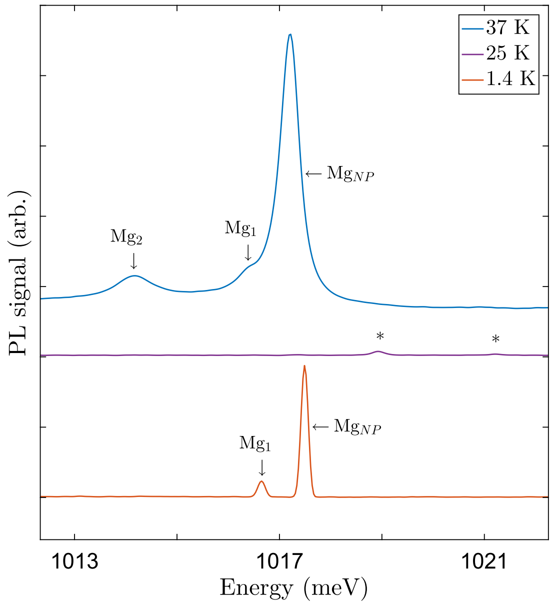

FIG. 3. Example spectra showing the Mg_{NP} line and associated features Mg_1 and Mg_2 in the high-, intermediate-, and low-temperature regimes. Two weak features labeled $*$ in the 25 K spectrum are of unknown origin. Spectra were collected at a resolution of 124 μeV with 1047 nm laser excitation.

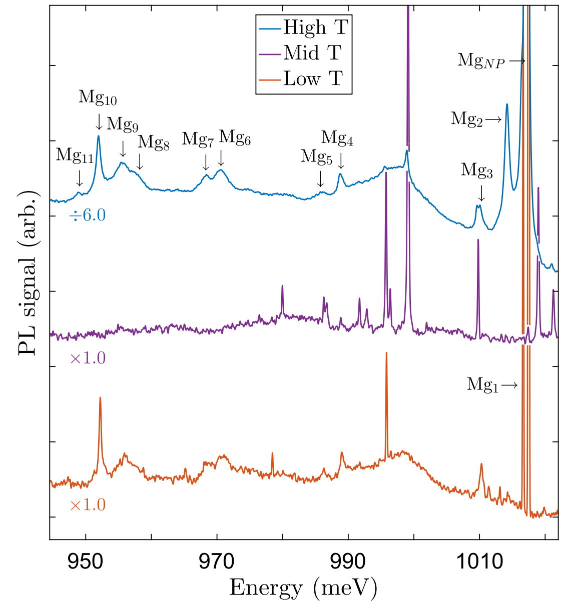

FIG. 4. PL spectra of the main Mg_{NP} line and a range of features below it in energy in three temperature regimes. For an improved signal-to-noise ratio we have averaged spectra at 35, 36, and 37 K to show the high-temperature regime. Similarly, spectra at 16, 20, and 25 K are averaged to show the middle regime, and spectra at 1.4 and 4.2 K are averaged to show the low-temperature regime. We note a number of features, labeled Mg_1–Mg_{11}, that display a temperature dependence similar to that of the main NP line that are likely related to the Mg-pair IBE. Many relatively narrow PL features of unknown origin, but with a different temperature dependence, most notable in the mid-T regime, are also observed but not labeled. The high-temperature spectrum has been scaled down by a factor of 6.0 to make the areas of the Mg_{NP} line in the high- and low-temperature spectra approximately equal for ease of comparison of the replicas. For both the high- and low-temperature spectra, the peak of the main Mg_{NP} line is truncated at the top edge of the plot, and the peak of the Mg_1 line in the low-temperature spectrum lies at the top edge of the plot. Spectra were collected at a resolution of 124 μeV with 1047 nm laser excitation. The temperature dependence of the Mg_1 and Mg_2 features relative to the Mg_{NP} line is better seen in Fig. 3.

B. Temperature dependence

Temperature dependence studies of the isoelectronic Mg pair center above 4.2 K show unusual behavior as summarized in Fig. 2. At liquid He temperatures, the Mg_{NP} line is strong and very sharp, allowing the isotopic fingerprint to be resolved at both 1.4 and 4.2 K, and a sharp line which we label Mg_1 can be observed 0.84 meV below the NP line. As 20 K is approached both the NP line and the Mg_1 line vanish, only to reappear above 30 K with substantially increased linewidth and intensity, together with a new feature downshifted from the NP line by 3.0 meV, which we label Mg_2. There is no sign of the Mg_2 line in the low-temperature spectra. Figure 3 compares the IBE spectrum at the three temperatures best illustrating this unusual behavior. Two weak features labeled $*$ in the 25 K intermediate temperature spectrum shown in Fig. 3 are of uncertain origin. The PL spectrum of this sample contains a number of weak, unidentified sharp features which may result from unintentional impurities introduced during the Mg-diffusion, and/or the complexes of such impurities with Mg. The rapid decrease in IBE PL intensity above ∼37 K, seen most clearly in Fig. 2(b), is very typical of IBE centers and results from thermal dissociation of whichever electronic particle, the electron or the hole, that is weakly bound by Coulomb attraction to the oppositely charged more tightly bound particle.

Specific phonon and LVM replicas are very characteristic of different IBE centers, and these have not been reported previously for the Mg-pair IBEs. This identification is complicated by the fact that the Mg-pair IBE luminescence in our sample does not dominate the PL spectrum as do many other IBE centers in optimized samples, and the PL spectrum of this Mg-diffused sample contains many unidentified weak but sharp lines. The replicas of the Mg_{NP} line are shown over a wider energy region in Fig. 4. Many unlabelled features, particularly in the intermediate-temperature spectrum where the Mg-pair IBE features vanish, likely result from other impurities introduced during the Mg diffusion or from complexes containing more than two Mg atoms.

The unusual temperature dependence of the Mg-pair IBE PL can be used to associate features which are replicas of the Mg_{NP} line, as already shown in Fig. 3 for the Mg_1 and Mg_2 lines, and reject unknown features which behave differently. In Table II we summarize the energy shifts of these lower-energy features which we believe are associated with the Mg-pair IBE. With a shift of only 0.84 meV, the Mg_1 feature is unlikely to result from a vibronic replica, but may instead originate in another electronic state of the Mg-pair IBE. The Mg_2 feature, which appears only in the high-temperature regime, has a shift which is more compatible with LVM replicas seen for other IBEs in silicon [15].

TABLE II. Energy shifts below the Mg_{NP} line of luminescence components which are believed to be related to the Mg-pair IBE. The Mg_{11} replica, which like Mg_2 is only observed in high-temperature spectra, likely results from the emission of the modes responsible for the Mg_2 replica plus the mode responsible for the Mg_{10} replica.

Label	Shift from Mg_{NP} (meV)
Mg_1	0.84
Mg_2	3.02
Mg_3	7.2
Mg_4	28.4
Mg_5	31.2
Mg_6	46.6
Mg_7	49.0
Mg_8	59.3
Mg_9	61.6
Mg_{10}	65.28
Mg_{11}	68.3

The strong Mg_{10} replica has a shift of 65.28 meV, very close to the 65.03 meV energy of the zone-center optical phonon energy measured using Raman scattering in these ^{28}Si samples.

The identification of Mg_3 as a replica of the Mg-pair IBE is tentative because an unknown line, seen in the intermediate temperature spectrum of Fig. 4, is superimposed on it. The Mg_{11} feature, which is observed only in the high-temperature spectra, may be a combination of the emission of the modes responsible for Mg_2 and Mg_{10}.

IV. CONCLUSION AND OUTLOOK

We have studied the PL spectrum of highly enriched ^{28}Si diffused with Mg to reexamine a luminescence line near 1017 meV previously observed in the PL spectrum of natural Si doped with Mg by Steinman and Grimmeiss [18] and proposed by them to be an IBE localized on a Mg-pair center. The isotopic fingerprint of this center made possible by the near-elimination of inhomogeneous broadening in ^{28}Si provides strong confirmation that the binding center of this IBE contains two Mg atoms. A number of lower-energy replicas of the main Mg_{NP} line were identified.

The behavior of the PL of this IBE center with changing sample temperature is very unusual and, to the best of our knowledge, is unique in Si. From pumped-He temperature to ~10 K there is little change in the spectrum, but from ~10 to ~17 K the intensity of all components decreases and vanishes from ~20 to ~30 K. Above ~30 K they reappear with increased intensity and NP linewidth, and a new replica downshifted by 3.02 meV appears which cannot be observed in the low-temperature spectrum. Above ~37 K all components decrease in intensity, and they disappear above ~50 K. This last behavior is familiar for all IBEs and results from the thermal dissociation of the weakly bound electronic particle of the IBE.

The disappearance of all IBE PL between ~20 and ~30 K, and its reappearance above ~30 K with increased intensity and NP linewidth, and with a new LVM replica, at present has no explanation. Further studies of the Mg-pair IBE would benefit from a careful optimization of the diffusion and annealing conditions which could maximize its intensity. Maximizing the total Mg concentration is known to not be optimal, because such samples have extremely weak PL, likely due to nonradiative recombination at Mg precipitates, as suggested by Steinman and Grimmeiss [18].

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