Donor bound excitons in Ge studied using photoluminescence excitation spectroscopy

1991 J. Phys.: Condens. Matter 3 4491

(http://iopscience.iop.org/0953-8984/3/24/017)

J. Phys.: Condens. Matter 3 (1991) 4491–4496. Printed in the UK

LETTER TO THE EDITOR

Donor bound excitons in Ge studied using photoluminescence excitation spectroscopy

A G Steele† and E C Lightowlers
Physics Department, King's College London, Strand, London WC2R 2LS, UK

Received 16 April 1991

Abstract. We report the first application of photoluminescence excitation spectroscopy to shallow donor bound excitons (BE) in Ge doped with As, P, or Bi. Transitions to the BE ground state and the first few excited states were observed by monitoring the longitudinal acoustic phonon replica of the principal bound exciton luminescence transition and scanning the laser excitation across the no-phonon region. Similar spectra were observed for Ge doped with each of the donors; an excited hole series, with states above the free exciton edge, was observed in each case. The energies of these states are in agreement with a simple hydrogenic model. From the apparent ionization limits and the bound exciton binding energies, an estimate of the D^- binding energy for each donor is made. The shallowest electron and hole excited states previously observed in infrared absorption measurements are also observed for the As bound exciton, and a comparison with these earlier results is made.

In the late 1970s, detailed studies of donor bound excitons (BEs) and bound multiexcitonic complexes (BMECs) in Ge were conducted using photoluminescence (PL) and near-infrared absorption spectroscopy [1–3]. Most of the observed transitions were interpreted using the Kirczenow shell model [4] which was very successful at describing both donor and acceptor BMECs in Si [5]. In the shell model, BE wavefunctions are constructed from properly antisymmetrized single particle wavefunctions, and the electron and hole states are labelled according to the irreducible representations of the T_d point group. In Ge, the lowest energy electron states (split by the valley–orbit interaction) transform as Γ_1 and Γ_5; the hole ground state transforms as Γ_8. Thus a donor BE (with two electrons and one hole) in the ground state is denoted by $\{2\Gamma_1;\Gamma_8\}$, and the first electron-excited state, where one of the electrons is promoted to the Γ_5 level, would be written as $\{\Gamma_1\Gamma_5;\Gamma_8\}$. Fine structure in this first BE electron-excited state manifold was observed in both photoluminescence as a multiplicity of the γ transitions ($\{\Gamma_1\Gamma_5;\Gamma_8\}\rightarrow\{\Gamma_5\}$), as well as of the corresponding δ transitions ($\{\Gamma_1\}\rightarrow\{\Gamma_1\Gamma_5;\Gamma_8\}$) observed in absorption [3]. This fine structure indicated the necessity of extending the shell model to include electron–electron and electron–hole interactions for Ge [6]. The first excited state for the donor BE in Ge is expected to be a p-like hole-excited state, $\{2\Gamma_1;\Gamma_x\}$, where the unidentified hole shell is labelled Γ_x [7]. The transition, labelled ϵ, between this state and the neutral donor ground state, has been observed in both PL and absorption [3]. Photoconductivity measurements

† Current address: Institute for Microstructural Sciences, National Research Council Canada, Ottawa, Canada K1A 0R6.

0953-8984/91/244491+06$03.50

[8,9] showed the existence of other, s-like, hole-excited states for the As and P BEs, which lie at energies above the free exciton (FE) edge. In this letter, we present the results of photoluminescence excitation (PLE) spectroscopy experiments on the As, P, and Bi donor bound excitons in Ge, identifying weak features in the spectra with the electron-excited state and the odd-parity hole-excited states previously observed in PL and absorption, as well as a well-defined hydrogenic series of s-like hole-excited states lying above the FE edge.

The material used in this study was Ge doped with As, P, or Bi, etched in HF–HNO_3, and polished using 1 μm diamond. The absorbing face was then polished with Syton. The doping concentrations were: [As] = 1×10^{15} cm^{-3}, [P] = 2.8×10^{15} cm^{-3}, and [Bi] = 1×10^{16} cm^{-3}. The samples were mounted in a He immersion cryostat, and pumped below the lambda point to 1.5 K. The excitation source was a Burleigh continuous wave Nd:YAG-pumped NaCl:OH$^-$ colour centre laser, which provided 250 mW of power. A $\frac{1}{2}$ m Spex monochromator was used to monitor the longitudinal acoustic (LA) phonon replica of the principal BE transition, while the laser excitation energy was scanned across the Ge no-phonon region. Since the resolution in this experiment is provided by the excitation source and not the spectrometer, the slits could be opened to 1 mm to maximize the signal intensity. A North Coast intrinsic Ge detector, cooled to 77 K, was used with standard lock-in amplification to detect the PL signal. The laser and spectrometer movement and the signal acquisition were computer controlled. Ordinary 4.2 K PL and 2 K absorption measurements on these samples were performed on a Nicolet 60SX Fourier transform spectrometer.

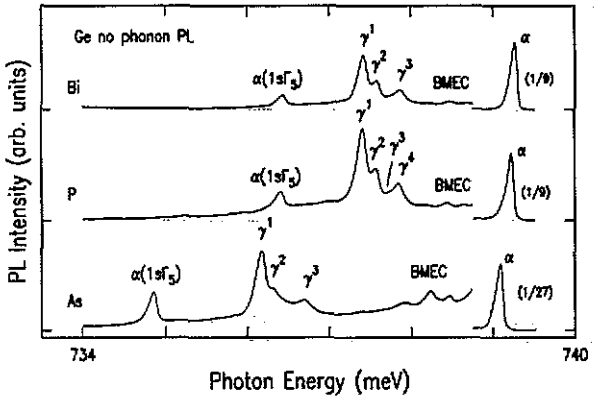

Figure 1. No-phonon PL spectra for Ge:As, Ge:P, and Ge:Bi collected at 4.2 K. All spectra are scaled to equal α peak height, and then rescaled as indicated.

Typical PL spectra collected in the no-phonon region for each of the donors are shown in figure 1, and an energy level diagram indicating the initial and final states of each transition for ease of comparison is shown in figure 2. The so-called principal BE lines (α) are transitions from the BE ground state to the neutral donor ground state, and have been scaled down as indicated. The lines labelled $\alpha(1s\Gamma_5)$ are transitions from the BE ground state to the donor $1s\Gamma_5$ excited state. The separation of this line from the α line gives the valley–orbit splitting for the donor. For As, P, and Bi, the valley–orbit splitting energies are 4.244 meV, 2.824 meV, and 2.839 meV, respectively. The γ^n transitions have the $\{\Gamma_1\Gamma_5;\Gamma_8\}$ excited state manifold of the BE as the initial

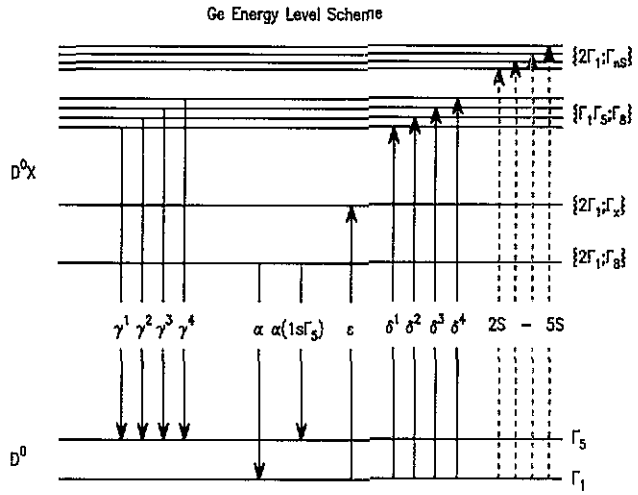

Figure 2. Energy level scheme for BE transitions using the labelling scheme appropriate to the Kirczenow shell model.

state; the final state is the $1s\Gamma_5$ neutral donor level. From these transitions, the splittings of the $\{\Gamma_1\Gamma_5;\Gamma_8\}$ manifold can be determined. Note that while there are 4 resolved components in the PL spectrum of P, only 3 components are observed for As and Bi. Calculations [6] for the As fine structure indicate that a fourth level should exist, and similarly one can expect additional levels for Bi. These levels are not observed in luminescence, but support for their existence may be found in the PLE spectra.

In absorption, some of the δ transitions from the neutral donor ground state have been observed in the LA phonon replica by Mayer and Lightowlers [2]. They suggested a parity selection rule for these transitions, which were not observed in the no-phonon region. As well as these electron excited states, the odd parity Γ_x level was observed in these studies via the ϵ transition, which could be seen in both phonon-assisted luminescence and absorption.

A comparison between PL and PLE spectra is made for Ge:As in figure 3. The energy scales have been adjusted to align the α transitions for the PLE and TA replica seen in PL with the $\alpha(1s\Gamma_5)$ transition in the no-phonon PL spectrum. This enables a straightforward comparison of features between the spectra. The first strong transition to an excited state in the PLE spectrum is the δ^2 transition, since it is shifted from the α line by an energy equal to the separation between the γ^2 and the $\alpha(1s\Gamma_5)$ transitions. Its extra width in PLE may be related to the presence of transitions to another level in the $\{\Gamma_1\Gamma_5;\Gamma_8\}$ manifold. The δ^1 line, as well as a shoulder due to δ^3 on the low energy side of the line labelled 2S, can also be observed as very weak features in the PLE spectrum. This is in agreement with the parity selection rule [2] since the oscillator strength for these transitions is clearly quite small. On the other hand, the δ^2 line has a much larger oscillator strength in the no-phonon region, as evidenced by its greater intensity in the PLE spectrum, while it is absent from the LA absorption spectrum of Mayer and Lightowlers. This suggests that a simple parity selection rule is insufficient to explain the transition probabilities. Also apparent in the PLE spectrum is the no-phonon ϵ transition, in good agreement with

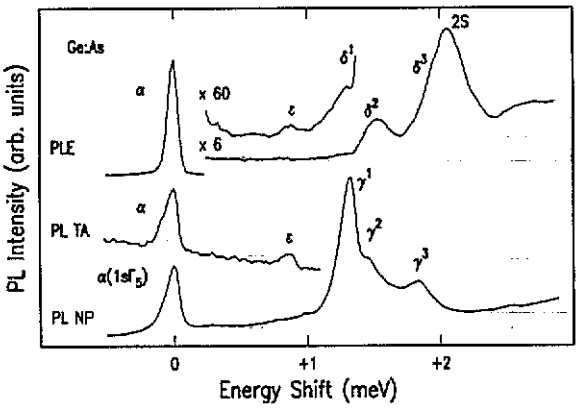

Figure 3. Comparison of Ge:As bound exciton excited states observed in PLE with transitions to corresponding energy levels as seen in PL. The energy scales have been shifted to align the indicated α transitions in each region.

the TA replica observed in PL. This same pattern is true for the P and Bi donors as well. The δ^3 line for P is strong in the no-phonon PLE spectrum and absent in the TA absorption spectrum. The strong δ line in the Bi spectrum lies between the second and third energy levels of the $\{\Gamma_1\Gamma_5;\Gamma_8\}$ manifold, indicating the presence of another, previously unobserved energy level for Bi. Higher resolution PL spectroscopy may be useful in identifying these proposed new levels for Bi and As.

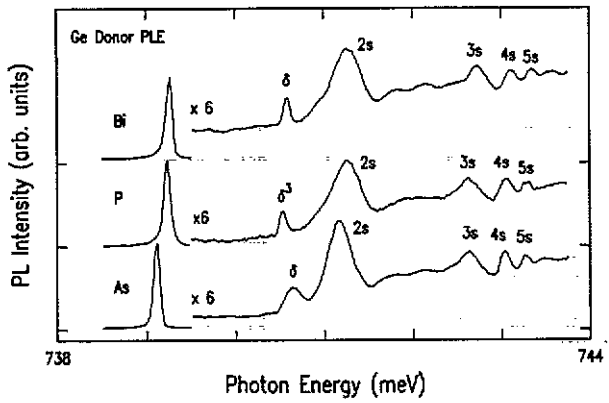

Figure 4. 1.5 K PLE spectra for Ge doped with As, P, and Bi collected by monitoring the PL intensity of the bound exciton LA phonon replica while scanning the laser excitation energy across the no-phonon region. The full width at half maximum for the As BE ground state is 0.09 meV.

Complete PLE spectra for the three different donors are shown in figure 4. The BE ground state transitions have been scaled to equal intensity, and the excited states are shown on a 6× expanded scale. The presence of a well resolved series of excited states for each of the donors is quite clear. The first three states for As and P were first observed in the photoconductivity experiments of Sokolov and Novikov [8] (their α, β, and γ transitions), and were assigned to hole excited states of the bound exciton.

From stress measurements on the line labelled 2S here, Gorbunov and Kaminskii [9] determined that the symmetry of the level must be Γ_8 if it were indeed an excited hole state.

The data presented show a clear similarity in the excited hole state series for all three donor species; there are corresponding transitions in each spectrum. Plotting the peak energy versus n^{-2} yields a straight line with apparent ionization limits approximately 4.48 meV, 4.42 meV, and 4.40 meV above the ground states for As, P, and Bi, respectively. This indicates that the hole states can be considered in a simple effective-mass model, where the highest observed transitions are not affected by the central cell potential of the donor. The large no-phonon absorption cross section would most likely point to an even parity state, hence the choice of S for labelling the states. These transitions are indicated on the energy level diagram of figure 2 by the broken lines. The width of these lines is probably due to lifetime broadening, since all of the states are well above the FE threshold and therefore, strictly speaking, represent resonances rather than bound states.

The hole ionization energies observed in PLE can be used to predict the D^- binding energies for each donor species. Adding the donor BE localization energy to the free exciton binding energy gives the energy of dissociation from a bound exciton to a neutral donor plus a free electron and a free hole. When the hole ionization energy is subtracted from this value, the D^- binding energy is obtained. The donor BE localization energies, found by subtracting the observed α no-phonon positions from the exciton gap energy of 740.46 meV [10], are 1.36 meV, 1.24 meV, and 1.19 meV for As, P, and Bi, respectively. The free exciton binding energy has only once been determined directly, by Sidorov and Pokrovskii [11], using far-infrared photoconductivity measurements, and they obtained a value of 4.15 meV. This is in close agreement with the theoretical calculations of Altarelli and Lipari [12] which yielded 4.18 meV. Combining these energies with our hole ionization energies gives As: D^- = 1.03 meV, P: D^- = 0.97 meV and Bi: D^- = 0.94 meV. From the onset of photoconductivity, Taniguchi and Narita [13] obtained As: D^- = 0.75 meV and Sb: D^- = 0.625 meV; the values for P and Bi would be expected to lie between these energies. A theoretical calculation by Weber and Oliveira [14] gave P: D^- = 0.61 meV, which is close to the experimental values obtained at high stress when both electrons are in the same conduction band valley [13]. The differences between our predictions and the direct experimentally determined D^- binding energies appear to be outside the range of the cumulative experimental errors, and could possibly be associated with ignoring complications arising from the ground state splitting of the free exciton at $k = 0$ [10, 15] and the extension in k space of the localized bound exciton state.

We have presented the first application of photoluminescence excitation spectroscopy to the study of shallow donor bound excitons in Ge. Several well resolved excited hole states are observed for excitons bound to As, P, and Bi donors, which can be treated in a simple effective mass picture. The D^- binding energies predicted from the apparent ionization limits of these series are somewhat higher than those determined in a limited range of photoconductivity measurements. Further experiments using perturbation techniques would be required to identify the symmetry of these hole excited states. The shallowest bound exciton excited states, which have been identified previously, are observed for the first time in the no-phonon region, due to the much higher excitation density afforded by the laser source over conventional absorption techniques. The existence of an additional level in the first electron-excited

manifold for As and Bi is suggested in analogy with the P bound exciton by the strong δ transition observed in PLE. This level lies between the levels currently denoted by 2 and 3, which necessitates increasing the indices for the As and Bi γ^3 and δ^3 transitions by unity.

This work was supported by the Science and Engineering Research Council. AGS thanks the Natural Sciences and Engineering Research Council of Canada for a NATO Research Fellowship.

References

[1] Mayer A E and Lightowlers E C 1979 *J. Phys. C: Solid State Phys.* **12** L539
[2] Mayer A E and Lightowlers E C 1979 *J. Phys. C: Solid State Phys.* **12** L945
[3] Mayer A E and Lightowlers E C 1980 *J. Phys. C: Solid State Phys.* **13** L747
[4] Kirczenow G 1977 *Can. J. Phys.* **55** 1787
[5] For a review of the properties of BMECs see
Thewalt M L W 1982 *Excitons* ed E I Rashba and M D Sturge (Amsterdam: North-Holland) pp 393–458
[6] Chang Y C and McGill T C 1982 *Phys. Rev.* B **25** 3945
[7] Pfeiffer R S and Shore H B 1981 *Solid State Commun.* **40** 165
[8] Sokolov N S and Novikov B V 1976 *Sov. Phys.–Solid State* **17** 2192
[9] Gorbunov M V and Kaminskii A S 1988 *Sov. Phys.–JETP* **68** 1453
[10] Mayer A E and Lightowlers E C 1979 *J. Phys. C: Solid State Phys.* **12** L507
[11] Sidorov V I and Pokrovskii Ya E 1973 *Sov. Phys.–Semicond.* **6** 2015
[12] Altarelli M and Lipari N O 1976 *Phys. Rev. Lett.* **11** 619
[13] Taniguchi M and Narita S 1977 *J. Phys. Soc Japan* **43** 1262
[14] Weber G and Oliveira L E 1989 *Phys. Status Solidi* b **151** 605
[15] Frova A, Thomas G A, Miller R E and Kane E O 1975 *Phys. Rev. Lett.* **34** 1572