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LETTER TO THE EDITOR

Bound-exciton luminescence and absorption in phosphorus-doped germanium

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Abstract. High-resolution absorption and luminescence spectra associated with the creation and decay of excitons bound to the neutral phosphorus donor in germanium are reported. The sharp line structure observed is analysed in terms of the Kirczenow shell model, which requires refinement to take account of the interparticle interactions in the excited state of the bound exciton.

During the past few years a considerable amount of attention has been devoted to the study of bound-exciton and bound multiexciton complexes in silicon lightly doped with the common substitutional donors and acceptors. These have been investigated mainly by means of the impurity-specific luminescence structure just below the exciton energy gap, which is associated with electron–hole recombination within the complexes. Most of the observed phenomena have been satisfactorily explained by the Kirczenow (1977a, b) shell model and recent developments have been reviewed by Thewalt (1978a). In marked contrast to the considerable attention which has been paid to silicon, only one fairly recent investigation of bound-exciton and bound multiexciton complexes in germanium has been described (Martin 1974). This work was performed before the introduction of the shell model and the luminescence structure observed could not be adequately explained. In this Letter we describe high-resolution absorption and luminescence spectra associated with the creation and decay of excitons bound to neutral phosphorus donors in germanium. The experimental data are analysed in terms of the shell model, which is seen to need refinement to take account of interparticle interactions.

The germanium samples used in this investigation were cut from a Czochralski-grown ingot, produced by the RSRE Electronic Materials Unit, with phosphorus concentrations between 1 and $4 \times 10^{21}\,m^{-3}$. The samples for luminescence studies, measuring $12 \times 6 \times 1\,mm^3$, were cut from the low-concentration end of the ingot and were etched in a solution containing 10% HF and 90% HNO_3 just before they were inserted in the cryostat. The sample for absorption studies was cut from the high-concentration end of the ingot and had a path length of 27 mm. The end faces were diamond-polished.

Luminescence was excited by the 647·1 nm line of a Kr ion laser, typically $\sim$300 mW defocused to $\sim$5 mm diameter, and was collected from the edge of the crystal. The sample was immersed in liquid helium and the bath temperature could be varied between 4·2 and 1·7 K by reducing the vapour pressure over the liquid. The sample temperature was always greater than that of the liquid, but the sample heating could be assessed by varying the laser power and by analysing the shape of the LA phonon-assisted free-exciton luminescence band (Mayer and Lightowlers 1979). For absorption measurements the sample was mounted strain-free in a Maeda-type helium flow cryostat (Maeda 1965) and the temperature was measured by a Au (0·03 % Fe)/Chromel thermocouple with the reference junction at 4·2 K. The radiation source was a high-stability vacuum tungsten strip lamp. The luminescence or transmitted light was dispersed by a Spex 1400 monochromator fitted with a 600 groove mm^{-1} grating blazed at 1·6 μm, and was detected by an intrinsic germanium diode detector cooled to 77 K (North Coast Optical Systems and Sensors EO-817).

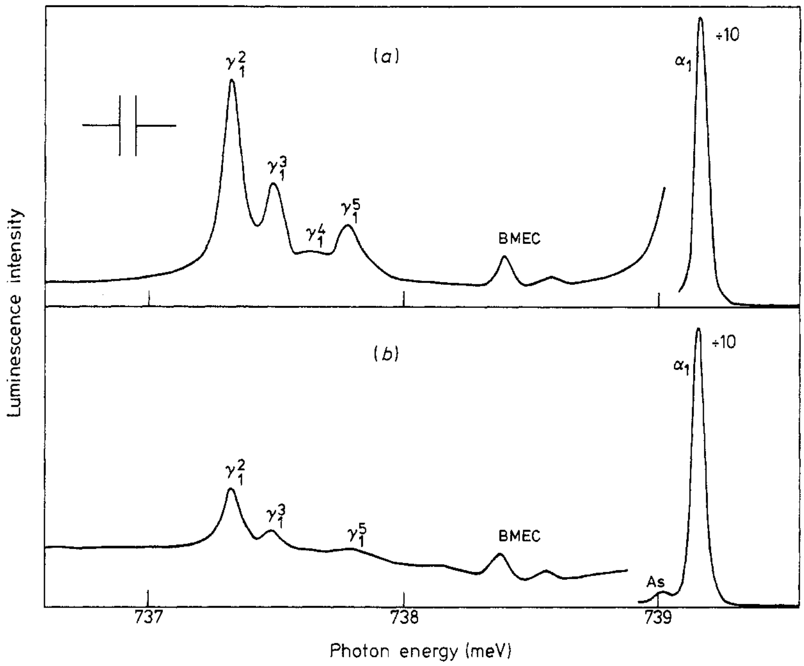

Figure 1. Luminescence spectra associated with the decay of excitons bound to neutral phosphorus donors in germanium. Data were obtained at 3·5 (*b*) and 5 (*a*) K in the no-phonon region. The ordinate axis is proportional to photons per unit energy interval. The lines are labelled with the transitions identified in figure 2. BMEC, bound multiexciton complex.

Luminescence spectra obtained in the no-phonon region at bath temperatures of 2·7 and 4·2 K are shown in figure 1. The estimated true temperatures are 3·5 and 5 K. These spectra are similar to that reported by Martin (1974) for Ge : P, but here the excitation density is much lower and the lines are better resolved. Martin considered that all of the features between the lowest- and highest-energy lines shown in figure 1 should be attributed to electron–hole recombination in bound multiexciton complexes. In order to differentiate clearly between the bound-exciton and bound multiexciton lines, we have investigated the relative intensities of all the lines as a function of excitation density. The spectra in figure 1 were obtained at the lowest excitation density consistent with a good signal-to-noise ratio and adequate resolution, and the bound multiexciton features make only a minor contribution. Except for the structure at ~738·5 meV, all of the other lines are associated with bound-exciton decay.

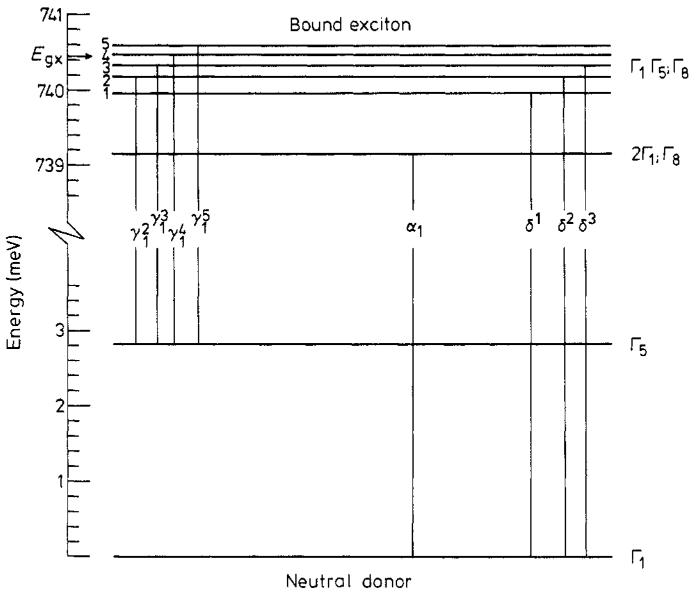

Figure 2. Energy level diagram for the neutral donor and donor-bound exciton based on the Kirczenow shell model. The luminescence and absorption lines associated with the transitions identified in the diagram are shown in figures 1 and 3 respectively. The energies on the upper part of the ordinate axis refer to the no-phonon region.

The most intense line at 739·16 ± 0·02 meV is identified with the α_1 transition in the shell model, in which a Γ_1 electron recombines with a Γ_8 hole in the lowest energy state $\{2\Gamma_1;\Gamma_8\}$ of the bound exciton to leave the neutral donor in the Γ_1 state (see figure 2). The weak line at 739·03 meV coincides with the position of the α_1 line for the arsenic donor. (Far-infrared absorption measurements on the material used for the luminescence studies have shown that arsenic donors are present at a concentration of $\sim 2\times 10^{19}\,m^{-3}$.) The group of four lines between 737 and 738 meV is identified with the γ_1 transition in the shell model, which involves the recombination of a Γ_1 electron and a Γ_8 hole in the $\{\Gamma_1\Gamma_5;\Gamma_8\}$ excited state of the bound exciton and leaves the neutral donor in the Γ_5 state. There is some evidence that in silicon, the $\{\Gamma_1\Gamma_{3,5};\Gamma_8\}$ bound-exciton state is split because of interparticle interactions (Lightowlers *et al* 1977, Elliott and McGill 1978), but the splitting is of a much smaller magnitude than that observed here for germanium. Measurements of temperature dependence have shown that the γ_1 lines thermalise with respect to the α_1 line, with activation energies close to the splitting of the bound-exciton state shown in figure 2. The corresponding absorption transitions in the no-phonon region, recorded at 12 K, are shown in the absorption spectra given in figure 3. This clearly demonstrates that these lines have no connection with bound multiexciton complexes.

The transitions labelled δ in figure 2 involve the recombination of a Γ_5 electron with a Γ_8 hole in the $\{\Gamma_1\Gamma_5;\Gamma_8\}$ bound-exciton state. The Γ_5 electron wavefunction vanishes at the donor ion and the Γ_8 hole wavefunction has a very small amplitude at the impurity site. Therefore, momentum cannot be conserved locally and the δ transitions should be observed only in the phonon-assisted spectra. The δ transitions have not been detected either in luminescence or absorption in the no-phonon region, but structure which can

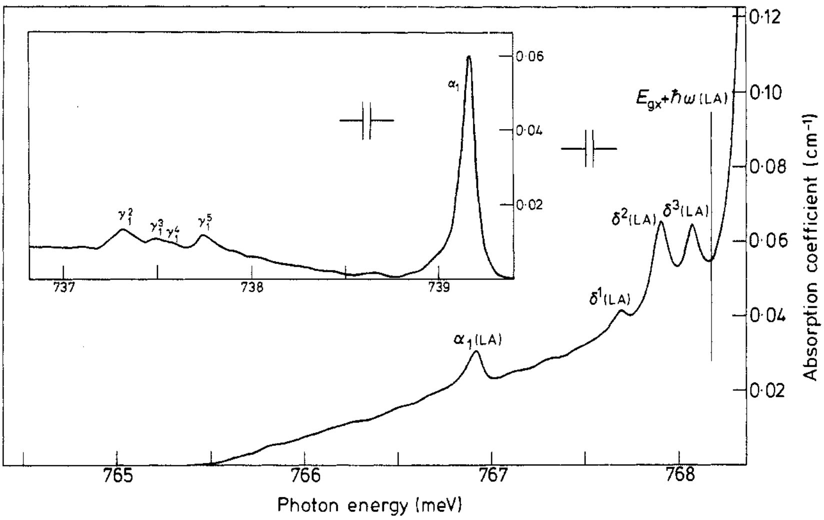

Figure 3. Absorption spectrum associated with the creation of excitons bound to neutral phosphorus donors in germanium. Data were obtained at ~7 K in the LA phonon-assisted region. The insert shows the absorption spectrum obtained at ~12 K in the no-phonon region. The two spectra are displaced by $(\hbar\omega)_{LA} = 27{\cdot}72 \pm 0{\cdot}04$ meV so that α_1 and α_1(LA) coincide, except for the 0·02 meV shift attributable to the temperature difference. The lines are labelled with the transitions identified in figure 2. Small ripples in both spectra are due to interference fringes.

be identified with δ^1 and δ^2 has been observed on the high-energy tail of the LA phonon-assisted free-exciton luminescence band. The intensity is low relative to that of the free-exciton band and the detector response falls rapidly in this spectral region. Consequently, the δ transitions have been studied primarily in absorption. The LA phonon-assisted absorption spectrum is shown in figure 3. The no-phonon and phonon-assisted spectra shown in the figure have been displaced by the LA momentum-conserving phonon energy $(\hbar\omega)_{LA} = 27{\cdot}72 \pm 0{\cdot}04$ meV so that α_1 and α_1(LA) coincide except for the 0·02 meV shift in energy attributable to the temperature difference (Mayer and Lightowlers 1979). The three lines observed close to the LA phonon-assisted absorption threshold are identified with the δ^1, δ^2 and δ^3 transitions shown in figure 2.

The energies of the emission and absorption lines observed are listed in table 1. Within the experimental errors quoted, the data are consistent with the valley–orbit splitting of the donor ground state $\Delta(\Gamma_1, \Gamma_5) = 2{\cdot}83 \pm 0{\cdot}02$ meV reported by Reuszer and Fisher (1964) and the momentum-conserving LA phonon energy quoted above, although a value of 27·75 meV for the latter would give a better fit. It should be noted that level 4 of the $\{\Gamma_1\Gamma_5; \Gamma_8\}$ bound-exciton state coincides almost exactly with the exciton energy gap $E_{gx} = 740{\cdot}46 \pm 0{\cdot}03$ meV (Mayer and Lightowlers 1979) and that level 5 lies in the free-exciton continuum. Any consequent broadening of the γ_1^4 and γ_1^5 lines is difficult to assess from the resolution-limited spectra presented here.

It is apparent from figure 2 that only two levels within the $\{\Gamma_1\Gamma_5; \Gamma_8\}$ manifold are clearly involved in both the δ and γ_1 transitions. From figure 1 it can be seen that a γ_1 transition involving level 1 must be at least an order of magnitude weaker than γ_1^2, and from figure 3 a δ^4 line would be discernible close to the free-exciton absorption threshold if the transition probability were similar to that of the other δ lines. A δ transition to level 5 would, however, be obscured by the absorption edge.

Although it is not possible at this stage to characterise the levels in the $\{\Gamma_1\Gamma_5;\Gamma_8\}$ bound-exciton state, it is clear that the multiplicity must be associated with interparticle interactions. An excited hole state has been invoked to explain additional structure observed in bound-exciton and bound multiexciton spectra from Si:Li (Thewalt 1978b, Henry and Lightowlers 1979) and has been suggested as a possible source of the small discrepancies in the energies of the δ and γ transitions from silicon doped with the group V substitutional donors (Thewalt 1978a). An excited hole state cannot account for the

Figure 1. Energies (meV) of the observed bound-exciton lines in the luminescence (5 K) and absorption (~7 K) spectra.

Luminescence		Absorption	
γ_1^2	737·33 ± 0·02	α_1 (LA)	766·91 ± 0·02
γ_1^3	737·47 ± 0·02	δ_1 (LA)	767·69 ± 0·02
γ_1^4	737·64 ± 0·04	δ^2 (LA)	767·91 ± 0·02
γ_1^5	737·76 ± 0·02	δ^3 (LA)	768·07 ± 0·02
α_1	739·16 ± 0·02		

fine structure observed here. It is apparent that in level 1, the Γ_5 electron and Γ_8 hole are closely correlated, leaving the Γ_1 electron to interact strongly with the donor ion and produce the lowest energy configuration. In level 4, and possibly level 5, the Γ_8 hole interacts more strongly with the Γ_1 electron than with the Γ_5 electron, which results in partial screening of the former from the positive ion core, thus weakening the binding of the complex. In levels 2 and 3, the Γ_8 hole interacts strongly with both the Γ_1 and Γ_5 electrons and both the δ and γ_1 transitions are allowed. It is likely that a similar splitting also occurs in silicon, but the energy separations between the levels are much smaller.

This investigation has shown that the Kirczenow shell model, which has been successful in describing bound-exciton and bound multiexciton spectra in silicon, can be applied to excitons bound to phosphorus donors in germanium. However, in contrast to silicon, interparticle interactions lead to easily detectable splitting of the excited state of the bound exciton. Similar structure has been observed in Ge:As, but the valley–orbit splitting of the donor ground state is larger than for phosphorus, which gives rise to a larger separation of the α_1 and γ_1 lines and enables the bound multiexciton lines to be studied in more detail.

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