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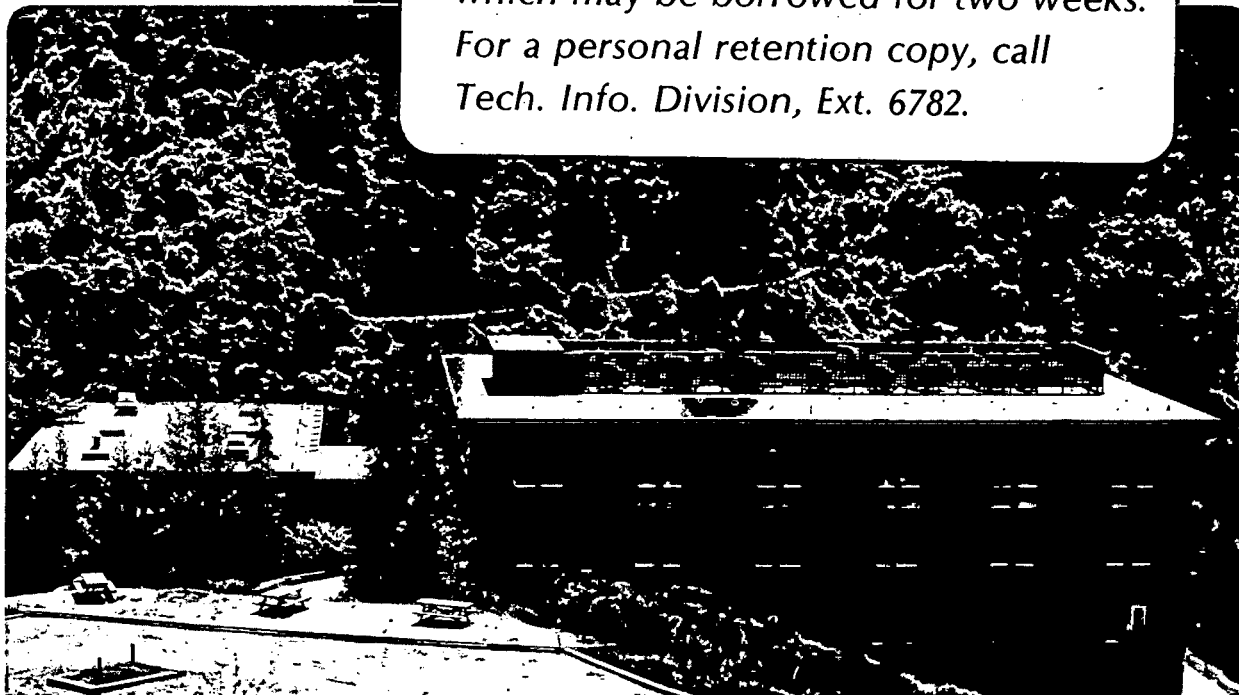
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G.A. Held, E.E. Haller, and C.D. Jeffries

May 1983

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Spectrally resolved luminescence associated with the decay of bound multiexciton complexes in optically excited Ge:Ga is observed. This is the first reported observation of multiexciton complexes in p-type germanium. The observed spectra are consistent with the shell model for bound multiexciton complexes.

No-phonon, TA, LA, and TO phonon assisted luminescence are observed. From these spectra, the energies of the LA, TA, and TO phonons in Ge:Ga are determined.

I. Introduction

The Kirczenow shell model¹ has been successful in accounting for most experimental observations of bound multiexciton complexes (BMEC's) in lightly doped silicon.² However, in germanium lightly doped with donors, Mayer and Lightowlers³ found that interparticle interactions result in splittings which cannot be explained by the present Kirczenow model. More recently, Lightowlers and Ciechanowska⁴ observed the luminescence and absorption spectra of bound excitons in p-type (acceptor doped) germanium. They observed a number of excited states of single bound excitons which cannot be explained with the present shell model. They also observed a three-fold splitting in the principal bound exciton (PBE) energy levels.

We present here observations of luminescence from PBE and BMEC's in Ge:Ga. As a result of probing lower energies than those reported by Lightowlers *et al.*,⁴ we have observed BMEC's consisting of up to five bound excitons in Ge:Ga.

II. Experimental

The germanium sample was cut from a large single crystal which had been grown along the (113) axis and has a gallium concentration of $1.1 \times 10^{15} \text{ cm}^{-3}$. The sample was lapped and polished with 3 μ alumina grit and etched with a 1:3 solution of HF:HNO₃. The final dimensions were 12 mm x 5 mm x 2 mm.

The sample was immersed in a temperature-regulated liquid helium bath and optically excited with 1.50 μ radiation. A 1000 watt feedback stabilized tungsten lamp, the output of which was passed through a 1.50 μ interference filter and then focussed onto the broadside of the crystal, was used as the source of optical excitation. At maximum excitation power the exciton density was still below the electron-hole liquid (EHL) condensation threshold. This technique of volume excitation (the penetration depth at 4°K is ≥ 1 mm) provided a significantly greater BMEC signal than excitation at just below EHL threshold from either a focussed or defocussed Ar laser beam.

The luminescence from the crystal edge was dispersed by a 0.25m Jarrel Ash spectrometer with a 590 groove/mm grating blazed at 1.2 μ m. The dispersed light was then detected with a liquid nitrogen-cooled, reverse-biased ultrapure germanium photodiode. By heating the photodiode

with a feedback stabilized resistor, we were able to extend the sensitivity of our detector to energies as low as 680 meV. The detector output was time integrated and digitized. All spectra were calibrated against the spectrum of a low pressure mercury discharge.

In order to improve the spectral resolution of our data, we deconvolved our spectra using the Jansson deconvolution algorithm.^{5,6} This iterative algorithm involves no assumptions about the locations, lineshapes, or number of peaks in the spectrum. The only information utilized is the spectrum and the spectrometer response function, which in our case was the observed spectrum of the 17327Å line of a low pressure mercury discharge. For a signal-to-noise ratio of better than 100:1 (our S:N was $\geq 350:1$), this algorithm has been shown to be very effective and reliable in improving resolution by a factor of 2-2.5 and clarifying spectral structure to the extent observed by us.⁶⁻⁹ It improved our resolution from 0.45 to 0.2 meV.

As a reliability test, after each iteration we reconvolved our deconvolved spectrum with our response function and compared the result with our original data. We found the deconvolution process to be convergent; after 80 iterations the reconvolved spectrum was not observably different from the original data. In summary, we conclude that our deconvolution has not introduced any spurious peaks in our spectrum. And, while all of the structure of the deconvolved spectrum can be discerned in the original data (with the exception of the 711.32 meV peak which, however, is also present in the luminescence spectra of Lightowers *et al.*⁴), it is only through the application of this deconvolution algorithm that the subsequent quantitative analysis of the BMEC energy levels has been possible.

III. Results and Discussion

For the no-phonon and phonon assisted spectra, the energies of the PBE luminescence peaks are shown in Table 1. Also recorded are the relative intensities of the phonon replicas and the energies of the TA, LA, and TO phonons (determined from the difference in energy between the phonon and no-phonon peaks). For the LA phonon, our value of 27.68 ± 0.03 meV is consistent with the 27.66 ± 0.02 meV result of Lightowers *et al.*,⁴ which they obtained by comparing the energies of phonon assisted absorption and luminescence. They did not report values for the other phonon energies.

Table 1. Energy of the most intense peak (PBE decay) for the no-phonon and phonon assisted luminescence spectra of Ge:Ga. Also, the phonon energies as determined from the energy differences of these lines. All energies ± 0.03 meV.

	Energy of Peak (meV)	Energy of Phonon (meV)	Relative Intensity
NP	739.48	-	1
TA	731.72	7.76	16
LA	711.80	27.68	170
TO	703.38	36.10	17

Our LA phonon assisted spectrum is shown in Fig. 1, and the energies of the peaks are listed in Table 2. Figure 2 displays the BMEC energy levels and the observed transitions. We have adopted Kirczenow's¹ notation in describing the electron and hole orbitals. Γ_{135} refers to the electron orbital of lowest energy. It consists of the Γ_1 , Γ_3 , and Γ_5 orbitals, whose splitting is negligible for acceptor BMEC's.¹ The Γ_{135} orbital therefore has a degeneracy of 12. Γ_8 refers to the hole orbital of lowest energy, which has a degeneracy of four, and Γ_x , the next lowest hole orbital, is of undetermined symmetry and degeneracy. A BMEC of size m consists of m electrons and $m+1$ holes bound to a single impurity site.

Table 2. Energies of the bound exciton and multiexciton lines in the LA phonon assisted luminescence spectrum of Ge:Ga (Fig. 1).

Transition	Energy, meV (± 0.03 meV)
1	711.80
2	711.32
3	710.87
4	710.42
5	709.98
6	709.14

Peak 1 of our spectrum (711.80 meV) corresponds to the decay of the PBE. It is our most intense peak, as is expected of the PBE line.

This peak has been observed by Lightowers et al.⁴ as a triplet in both luminescence and absorption measurements (we were unable to resolve this fine splitting). The presence of this transition in absorption spectra implies that in luminescence its final state is the Γ_8 neutral donor. That within the absorption spectrum this is the peak of lowest energy confirms that it is the PBE peak.

Lightowers et al.⁴ have observed excited bound excitonic structure in the 712-713 meV region in absorption and luminescence studies. We also observed this excited state structure, as well as the free exciton line at 713.1 meV, at 4.2°K. However, at 2°K these peaks were not observable, as almost all the excitons were in the more stable bound states.

Peak 2 of our spectrum is not observed by Lightowers et al.⁴ in their absorption spectra; it therefore corresponds to one of the following two transitions:

$$\Gamma_{135}; \Gamma_8\Gamma_X \rightarrow \Gamma_X + \text{phonon} + \text{photon}$$

$$2\Gamma_{135}; 3\Gamma_8 \rightarrow \Gamma_{135}; 2\Gamma_8 + \text{phonon} + \text{photon}.$$

We believe it to be the second of these transitions for the following reasons. The intensity ratio of the two peaks, 2:1, is found to decrease as the temperature of the sample is increased from 1.7°K to 4.2°K. This observation is consistent with an $m=2$ initial state for peak 2 but contradicts what one would expect if the initial state were a single excited bound exciton.

Moreover, it is unlikely that any of our observed transitions are from excited initial states (i.e., $\Gamma_{135}; \Gamma_8\Gamma_X$, $2\Gamma_{135}; 2\Gamma_8\Gamma_X$, $3\Gamma_{135}; 3\Gamma_8\Gamma_X$, or $4\Gamma_{135}; 3\Gamma_82\Gamma_X$). If any peak in our spectrum were due to the decay of one of these excited states, it would be weighted by a Boltzmann factor of less than 0.08 relative to the peak resulting from the decay of the corresponding ground state ($\Gamma_{135}; 2\Gamma_8$, $2\Gamma_{135}; 3\Gamma_8$, $3\Gamma_{135}; 4\Gamma_8$, and $4\Gamma_{135}; 4\Gamma_8\Gamma_X$). Since none of the observed peaks exhibit such a strong thermalization, we conclude that peaks 1, 2, 3, and 4 are as shown in Fig. 2.

The Γ_8 orbital has a degeneracy of four, and thus the $m=4$ ground state must be of the form $4\Gamma_{135}; 4\Gamma_8\Gamma_X$. From this state one would expect to observe both of the following transitions:

$$4\Gamma_{135}; 4\Gamma_8\Gamma_X \rightarrow 3\Gamma_{135}; 4\Gamma_8 + \text{phonon} + \text{photon}$$

$$4\Gamma_{135}; 4\Gamma_8\Gamma_X \rightarrow 3\Gamma_{135}; 3\Gamma_8\Gamma_X + \text{phonon} + \text{photon}.$$

For either of these transitions to have an observable no-phonon replica, the decaying hole must be strongly localized at the impurity site (where crystal momentum is not conserved). Because the Γ_8 orbital is localized at an impurity site, one would expect the transition

$$4\Gamma_{135}; 4\Gamma_8\Gamma_X \rightarrow 3\Gamma_{135}; 3\Gamma_8\Gamma_X + \text{photon}$$

to be observed. However, if the Γ_X orbital is of p-type symmetry, as was observed by Mayer and Lightowlers¹⁰ for donor bound excitons, one would expect the transition

$$4\Gamma_{135}; 4\Gamma_8\Gamma_X \rightarrow 3\Gamma_{135}; 4\Gamma_8 + \text{photon}$$

to be forbidden. Unfortunately, our signal-to-noise ratio in the no-phonon region was not large enough to establish which of these LA assisted peaks has a no-phonon replica. For this reason, our assignment of peaks 5 and 6 is just reasonable speculation based on previous studies of donor bound excitons in Si¹¹ and Ge.¹⁰ It is possible that our assignments of peaks 5 and 6 should be reversed. It is also possible that peak 6 corresponds to the transition

$$6\Gamma_{135}; 4\Gamma_83\Gamma_X \rightarrow 5\Gamma_{135}; 4\Gamma_82\Gamma_X + \text{phonon} + \text{photon}.$$

Better signal-to-noise in the no-phonon region will be required before any definitive assignments of these lower energy transitions can be made.

In conclusion, we have observed BMEC's consisting of up to five bound excitons in p-type germanium. Our observations are consistent with the Kirczenow shell model.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

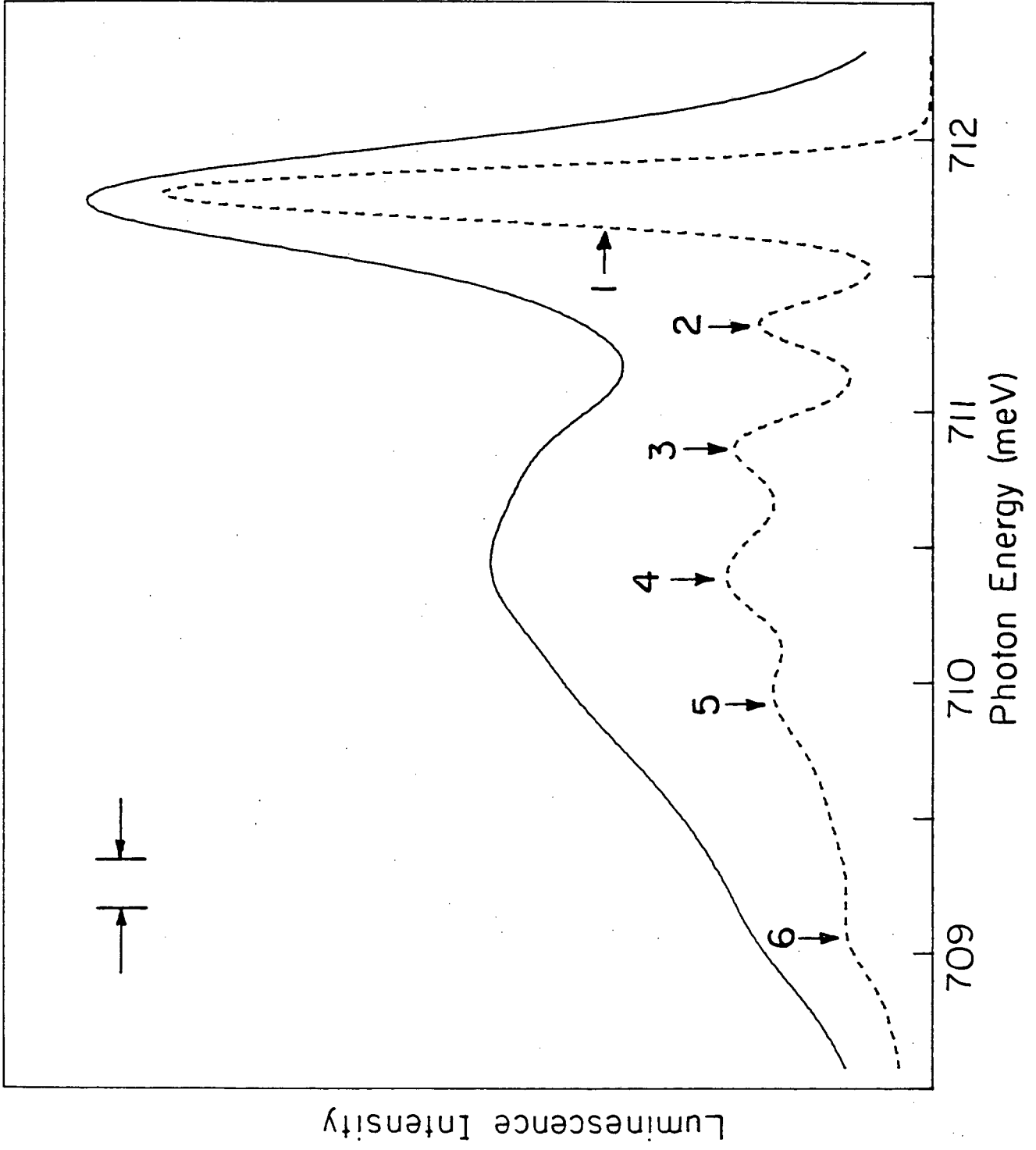
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Figure Captions

Figure 1 - The 2°K photoluminescence spectrum of Ge:Ga in the LA phonon assisted region. The excitation source was a 1000 watt feedback stabilized tungsten bulb, the output of which was passed through a 1.50 μ interference filter. The impurity concentration was $1.1 \times 10^{-15} \text{ cm}^{-3}$. The solid curve shows the original data and the dotted curve shows the deconvolved spectrum. The resolution shown is that of the deconvolved spectrum.

Figure 2 - Energy level diagram for BMEC's in Ge:Ga. m labels the number of excitons bound to a single impurity (m electrons, $m+1$ holes). The luminescence peaks associated with the transitions identified in the diagram are shown in Fig. 1.



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Figure 1

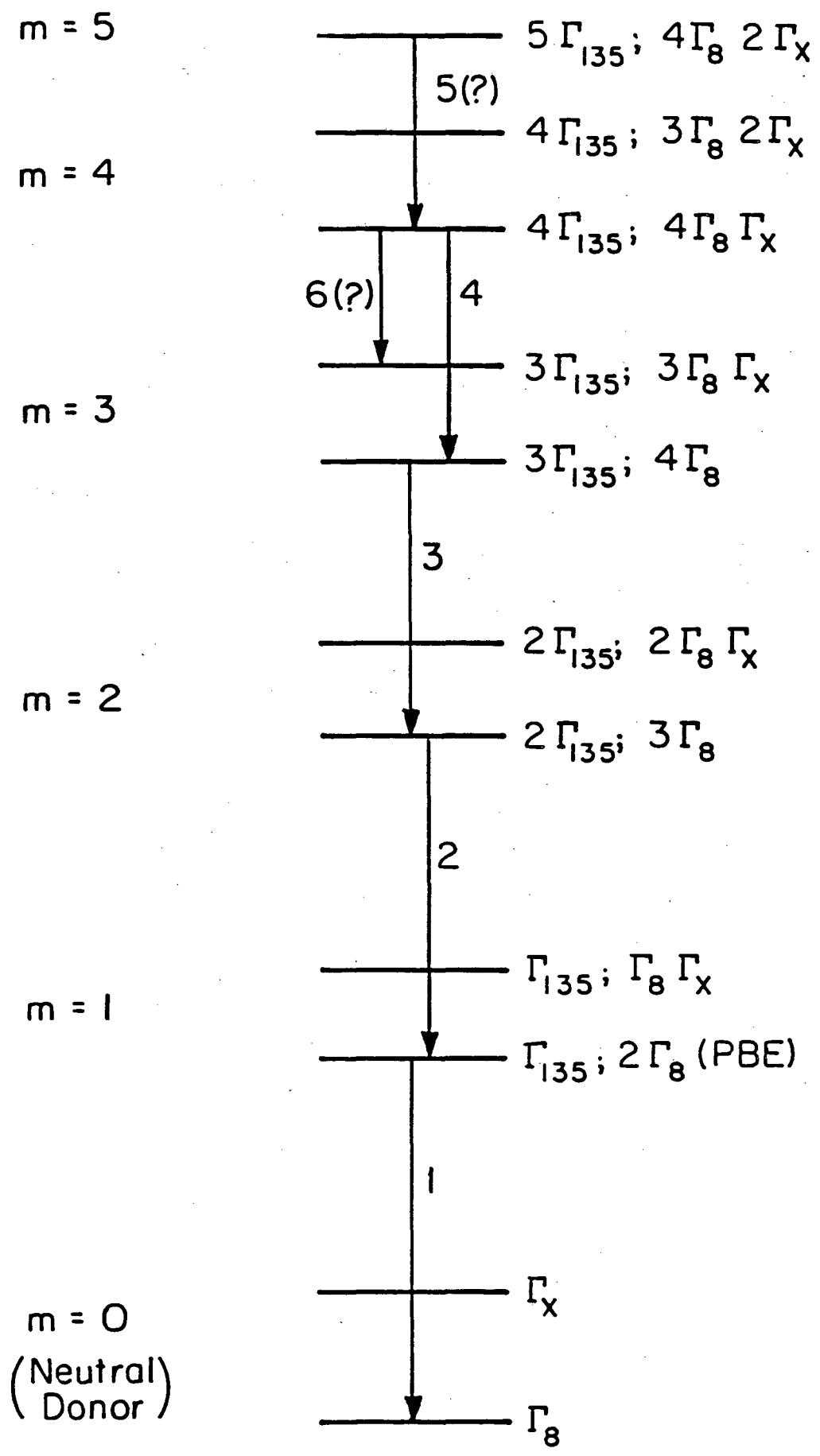


Figure 2

XBL834-5569

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