RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 11 15 APRIL 1990-I

# Photoluminescence from excitons bound to a triple acceptor, Ge:Cu

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(Received 11 December 1989)

We report the first observation of a triple-acceptor bound exciton, revealed in the photoluminescence spectrum of Cu-doped Ge, and verified by a two-hole replica series having the known Cu ionization energy. High-resolution photoluminescence reveals a finely split doublet independent of Cu isotopic species. This is an unexpected result, since present models of both the triple acceptor and its bound exciton predict that neither ground state should have any fine structure.

Substitutional group-IIIA impurities in silicon and germanium form single acceptors and effective-mass theory has been extremely successful in describing their electronic levels.[1] It is also well known that group-II substitutional impurities in germanium form double acceptors, examples being Ge:Zn, Ge:Hg, Ge:Be, and Ge:Mg.[1,2] The primary difference between the electronic levels of single and double acceptors lies in the nature of the ground states. It was found that the double-acceptor ground state could be described by combining two antisymmetric single-acceptor ground states in a manner similar to the central-field approximation of atomic physics.[3] Each hole is treated as moving in the field of the negative core and in the average potential arising from interactions with the other hole. These hole-hole interactions result in observable splittings in the double-acceptor ground states, whereas the excited states remain well described by single-hole excitations. By further extending this simple picture of the electronic character of impurities in a group-IV semiconductor to substitutional group-I impurities, one expects that these should be triple acceptors and could also, under certain circumstances, be described by the central-field approximation.

Copper in germanium, in addition to being an important material for midinfrared (MIR) detectors, has long been considered to be the prototypical triple acceptor.[4–8] The binding energies of its odd-parity excited states are extremely close to those of single acceptors,[8] leading investigators to model its ground state using the methods outlined above. While this approach has met with some success, the electronic properties of the copper triple acceptor are still not well understood. Until now the optical spectroscopy of this center has been limited to MIR absorption studies of the electronic transitions from the acceptor ground state to the odd-parity excited states.[6–8] A complementary method of studying the ground state is photoluminescence (PL) spectroscopy, since the final state of the principal luminescence transition is the ground state of the neutral acceptor. We present here PL spectra from Ge:Cu. This is the first reported observation of luminescence from the decay of excitons bound to a triple acceptor in any semiconductor.

The ground-state wave function of the bound hole in a neutral acceptor is described by the fourfold-degenerate irreducible representation $\Gamma_8$ of the double group $\bar{T}_d$.[1] By taking the antisymmetric direct product of two single-hole wave functions, the double-acceptor ground state is then given by $\{\Gamma_8\times\Gamma_8\}=\Gamma_1+\Gamma_3+\Gamma_5$.[2,3,9] The Ge:Hg ground state has long been recognized to be split by these hole-hole interactions[2] and recent PL and FIR studies have shown similar splittings for the other double acceptors.[3] Extending the central-field approximation leads to a ground state of the neutral triple acceptor given by the antisymmetric direct product of three single-hole ground states, $\{\Gamma_8\times\Gamma_8\times\Gamma_8\}=\Gamma_8$.[7,8] This ground state is a single unsplit level in the absence of external perturbations. Salib, Fisher, and Simmonds,[8] following the successful work of Kartheuser and Rodriguez[9] on double acceptors, further extended this model to predict the relative intensities and splittings of the MIR absorption lines under uniaxial stress. With the assumption that the stress-induced splitting of the triple-acceptor ground state was also present in the excited states, some agreement with the observed splittings under uniaxial stress was achieved, but problems remained with the relative intensities and the thermalization behavior of the lines. The most striking difficulty was the observation of forbidden transitions from the thermally populated, stress-split ground state. We have also studied the Ge:Cu triple-acceptor MIR absorption versus stress and temperature, but have not yet succeeded in finding a consistent model for the results.

When an exciton is localized on such a neutral triple acceptor, the electronic system would consist of the four holes in a spin singlet, and one electron which is thus left unable to couple to the holes. In the language of Kirczenow's shell model[10] this represents the closing of the first hole shell. The triple-acceptor bound exciton (BE) is thus also predicted to have a simple unsplit ground state. The results presented here show that the principal BE ground state to neutral-acceptor ground-state luminescence is in fact a doublet, and hence either the BE ground state or the neutral triple-acceptor ground state is unexpectedly split. We present evidence that suggests that the splitting is in the acceptor ground state.

The samples used in the present study were cut from ultrahigh purity (UHP) germanium with low dislocation density. A barely visible layer of pure copper was evaporated onto the samples and then diffused in at temperatures ranging from 450 to 800 °C for periods of 1–24 h, rapidly followed by quenching in ethanol. The diffusion was performed in a helium atmosphere. The samples were then left to soak in dilute nitric acid for at least 1 h to re-

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move excess copper from the surfaces. This cleaning was followed by standard polishing and etching to obtain surfaces suitable for PL measurements. The PL was excited with an $Ar^+$ ion laser at powers ranging from 100 mW to 1 W. The spectroscopy was performed on Fourier-transform interferometers, a Bruker IFS 113v and a Bomem DA3.01, with a liquid-nitrogen-cooled Cincinnati Electronics IDH-100 InSb detector. The high sensitivity of the interferometers was essential for the observation of the weak luminescence signal. All measurements were made with the sample immersed in liquid helium at temperatures ranging from 1.6 to 4.2 K.

Figure 1 shows spectra as a function of the diffusion temperature. At the bottom [Fig. 1(a)] is a spectrum from the untreated UHP Ge. Above this are spectra obtained from samples into which the copper was diffused at 500 °C [Fig. 1(b)], 600 °C [Fig. 1(c)], and 800 °C [Fig. 1(d)] corresponding to Cu concentrations of $1\times10^{13}$, $3\times10^{14}$, and $1.5\times10^{16}$ $cm^{-3}$, respectively.[4] The spectrum from the untreated sample shows no sign of the features attributed to Cu which are clearly evident in all of the other spectra. In the sample prepared at 500 °C [Fig. 1(b)], new transitions appear in the no-phonon (NP), the longitudinal-acoustic (LA) phonon replica, and the transverse-optical (TO) phonon regions. These lines are labeled $Cu_{NP}$, $Cu_{LA}$, and $Cu_{TO}$, respectively. At this concentration the $Cu_{NP}$ and $Cu_{LA}$ remain much weaker than the LA-phonon-assisted free-exciton (FE) line, labeled $FE_{LA}$. In the spectrum from the sample prepared at 600 °C [Fig. 1(c)] the $Cu_{NP}$ line is comparable in intensity to the $FE_{LA}$ line, and the transverse-acoustic (TA) phonon replica $Cu_{TA}$ has become apparent. At higher diffusion temperatures the $Cu_{NP}$-to-$FE_{LA}$ intensity ratio continues to increase, but the overall luminescence intensity becomes prohibitively small. Since each spectrum shown here is scaled to the same maximum peak height, this decrease in overall luminescence intensity is evident in Fig. 1(d) by the increased noise in the spectrum obtained from the 800 °C sample. Samples prepared between 600 and 650 °C were found to be optimal, having strong enough Cu features without sacrificing too much signal. It should be noted that the exact ratio of the $Cu_{NP}$-to-$FE_{LA}$ lines is also a sensitive function of the quench rate and subsequent thermal history. A fast quench was found to be essential in maximizing the PL, as was avoiding any later heating of the samples, although storage at room temperatures presented no problems. The high mobility of Cu as an interstitial and its tendency to precipitate at dislocations[11] are probably responsible for this behavior and undoubtedly contribute to the weak luminescence.

Unambiguous identification of the PL with the Cu triple acceptor was allowed by the observation of the NP two-hole transitions just below the optical-phonon replica region. These transitions leave the neutral acceptor in an excited even-parity state and are shown in the low-noise spectrum of Fig. 2. The intensity of the $2S$ line is approximately $\frac{1}{50}$ that of the principal NP BE line. Using the observed energies of the $3S$, $4S$, and $5S$ two-hole transitions in a hydrogenic level scheme, an ionization energy of $E_i = 43.26 \pm 0.03$ meV was obtained. The $2S$ transition was omitted because central-cell effects were still evident. This result is in excellent agreement with the value of $E_i = 43.25 \pm 0.01$ meV from the MIR absorption of Salib *et al.*,[8] confirming that the luminescence is from the neu-

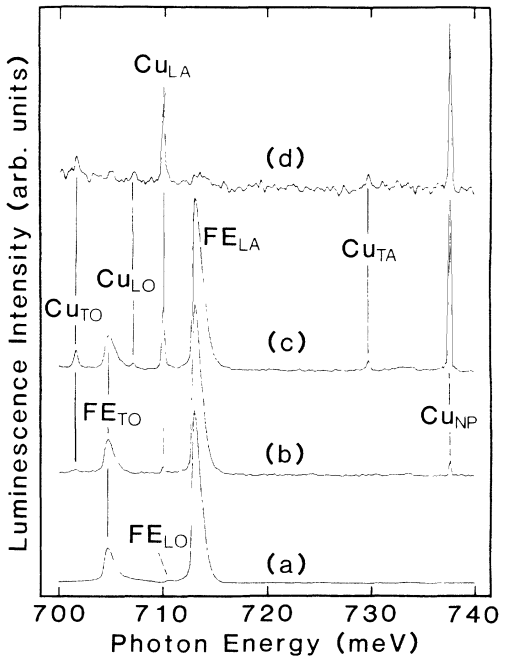


FIG. 1. Ge:Cu PL spectra taken at 4.2 K showing the NP and phonon replica regions as a function of Cu concentration or diffusion temperature. The Cu concentrations for the top three spectra are, from top to bottom, $1.5\times10^{16}$, $3\times10^{14}$, and $1\times10^{13}$ $cm^{-3}$ corresponding to diffusion temperatures of 800, 600, and 500 °C. The bottom spectrum (d) is from the UHP Ge starting material. The apodized resolution is 0.37 meV.

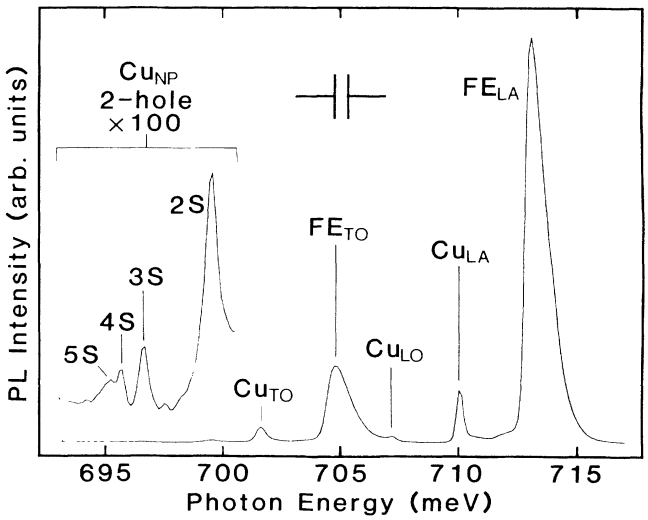


FIG. 2. A low noise Ge:Cu PL spectrum at 4.2 K, showing the phonon replicas and, on an expanded vertical scale, the NP two-hole transitions. Resolution is 0.37 meV. At this resolution the peak height of the NP $2S$ transition is approximately $\frac{1}{50}$ that of the NP principal transition. Cu diffusion was performed at 600 °C.

tral triple-Cu acceptor.

The bound exciton PL is strongest in the NP region, and at high resolution (Fig. 3) the principal NP transition from the BE ground state to the neutral-acceptor ground state was always observed to be split into a pair of well-resolved lines at 737.69 and 737.75 meV. Both the extremely small separation and the intensity ratio of the two components initially suggested that the splitting might be related to a copper-isotope effect. The natural isotopic abundance of copper is 69.09% $^{63}$Cu and 30.8% $^{65}$Cu. Spectra obtained from a sample doped with 99% isotopically pure[12] $^{63}$Cu are shown in Figs. 3(b) and 3(c). Since both transitions occur in the isotopically pure sample, the splitting cannot be isotope related. If these were transitions from two levels of a split BE ground state in thermal equilibrium, lowering the sample temperature would change the relative intensity of the peaks. Within the signal-to-noise ratio currently achieved, no thermalization was observed when the liquid-helium bath temperature was decreased from 4.2 to 1.6 K [Figs. 3(b) and 3(c)], even when the excitation power was reduced to very low levels to avoid sample heating. Assuming that the sample temperature equaled the bath temperature, a small change in the relative intensities of the lines should have been observable over this temperature range if the splitting originated in the initial state of the transition. This suggests that the splitting reflects the final state of the BE transition, the ground state of the neutral triple acceptor. This splitting is unexpected and may provide information leading to a more complete understanding of triple acceptors. The piezospectroscopy of the PL is currently being studied and the results will be published at a later time.

Taking the FE energy of 740.46 meV reported by Mayer and Lightowlers,[13] we obtain an exciton localization energy of 2.77 meV for the Cu BE. While this is greater than the exciton localization energies of the shallow single acceptors in Ge, it is much less than the exciton localization energy of the double acceptors Zn, Mg, and Be, all of which are shallower acceptors than Cu. This low-exciton localization energy for Cu is initially surprising, but is consistent with the results of McMurray[14] on the $A^+$ hole binding energies of multiple acceptors in Ge.

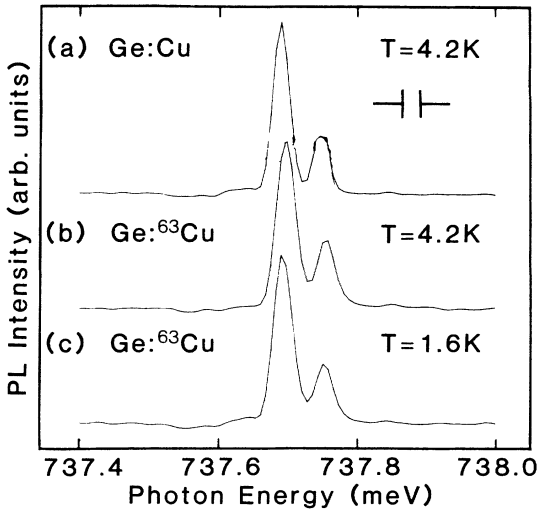


FIG. 3. High-resolution spectra of the split no-phonon principal BE transition of Ge:Cu prepared with (a) natural copper and (b), (c) 99% isotopically pure $^{63}$Cu. The latter two also show the effect on lowering the He bath temperature from 4.2 to 1.6 K. Resolution is 0.023 meV.

In conclusion, we have observed the first photoluminescence from excitons bound to a triple acceptor, Cu in Ge. High-resolution spectra reveal a fine splitting of the no-phonon BE line which appeared not to thermalize and did not depend on the isotope of copper present. There is, at present, no model for this unexpected splitting. Further work will be necessary to elucidate the true nature of the ground state.

This work was supported by the Natural Sciences and Engineering Research Council of Canada and M.K.N. is grateful for additional support from the Advanced Systems Foundation of British Columbia. We also thank E. E. Haller for providing the ultrahigh purity germanium.

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[1]For a review, see A. K. Ramdas and S. Rodriguez, Rep. Prog. Phys. **44**, 1297 (1981).

[2]R. A. Chapman and W. G. Hutchison, Phys. Rev. **157**, 615 (1967).

[3]For a recent review of spectroscopy of double acceptors see M. L. W. Thewalt, D. Labrie, I. J. Booth, B. P. Clayman, E. C. Lightowlers, and E. E. Haller, Physica B+C **146**, 47 (1987).

[4]H. H. Woodbury and W. W. Tyler, Phys. Rev. **105**, 84 (1957).

[5]W. J. Moore, Solid State Commun. **3**, 385 (1965).

[6]N. R. Butler and P. Fisher, Phys. Lett. **47A**, 391 (1974).

[7]E. H. Salib, K. J. Duff, P. Fisher, and P. E. Simmonds, Solid State Commun. **44**, 81 (1982).

[8]E. H. Salib, P. Fisher, and P. E. Simmonds, Phys. Rev. B **32**, 2424 (1985).

[9]E. Kartheuser and S. Rodriguez, Phys. Rev. B **8**, 1556 (1973).

[10]G. Kirczenow, Can. J. Phys. **55**, 1787 (1977).

[11]A. G. Tweet, Phys. Rev. **106**, 221 (1957).

[12]$^{63}$Cu was obtained from *Icon Services Inc.*, 19 Oxbow Lane, Summit, NJ 07901.

[13]A. E. Mayer and E. C. Lightowlers, J. Phys. C **12**, L507 (1979).

[14]R. E. McMurray, Jr., Solid State Commun. **53**, 1127 (1985).