# Piezospectroscopy of the ground and excited states of zinc double acceptors in germanium

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(Received 15 June 1987; revised manuscript received 25 January 1988)

Piezospectroscopic midinfrared absorption studies of the neutral double acceptor Zn in Ge have been undertaken to determine the ordering and symmetries of the ground and excited states. The results are shown to be in excellent agreement with existing theoretical models of the double acceptor states, provided that the lowest-energy component of the split ground state has $\Gamma_1$ symmetry at zero stress. The experimentally determined deformation-potential constants for Zn agree well with those of the single acceptor Ga in Ge.

## I. INTRODUCTION

While it has long been known that the ground state of the deep double acceptor Hg in Ge is split due to hole-hole interactions,[1-3] it was thought that these effects were unimportant for shallower species. More recent studies of shallow double acceptors in Ge have, however, lead to the observation of a ground-state splitting for Be, Zn, and Mg.[4] The first such observation was made by Cross *et al.*[5] who detected small line splittings in the absorption spectrum of Ge:Be. They interpreted their results by considering the symmetry of the single- and double-acceptor ground-state wave functions where the former transforms as $\Gamma_8$ of the double group $\overline{T}_d$ and the latter transforms as the antisymmetric direct product of two such states:

$$\{\Gamma_8\times\Gamma_8\}=\Gamma_1+\Gamma_3+\Gamma_5\ . \tag{1}$$

They attributed the ground-state splitting to a lifting of the degeneracy of the ground-state multiplet due to the hole-hole interaction, leading to three levels, $\Gamma_3$, $\Gamma_5$, and $\Gamma_1$. By making an analogy with atomic systems, which was quite general in the existing literature on double acceptors, they located the $\Gamma_1$ ($J=0$) level higher in energy than the $\Gamma_3+\Gamma_5$ ($J=2$) levels.

Thewalt *et al.*[6] observed an unexpectedly large ground-state splitting of $2.4\pm0.1$ meV in Ge:Zn which was also attributed to hole-hole coupling. By comparing the double-acceptor system with that of an exciton bound to a single acceptor in Si, they proposed that the lowest double-acceptor ground state might in fact have $\Gamma_1$ symmetry. This was supported by a uniaxial stress study of the photoluminescence of bound exciton and bound multiexciton complexes in Ge:Zn.[4] Recently, however, Binggeli and Baldereschi[7] reported a theoretical calculation of the ground-state splitting of Ge:Zn which indicated that the $\Gamma_3+\Gamma_5$ state was more tightly bound than $\Gamma_1$.

The object of the present paper is to verify the symmetry and ordering of the ground and excited states of the Zn double acceptor in Ge by piezospectroscopic studies of the midinfrared (MIR) absorption lines. Preliminary uniaxial stress measurements in Ge:Zn were made by Fisher *et al.*[8] and were tentatively explained by Kartheuser and Rodriguez[9] using a model in which a fully degenerate ground state was assumed at zero stress. In the present study we extend the model of Kartheuser and Rodriguez to include a large ground-state splitting due to the hole-hole interaction. Using this model, excellent agreement is obtained between theory and experiment leading us to the identification of the lowest ground state as $\Gamma_1$. Furthermore, the values of the deformation-potential constants of Ge:Zn derived in this work agree closely with those of the single-acceptor system Ge:Ga.[10]

In Sec. II we describe the experimental techniques used to measure the absorption spectrum of Ge:Zn as a function of stress, temperature, and polarization of the MIR radiation. The experimental results are given in Sec. III along with a theoretical analysis. The results presented in this paper are then summarized in Sec. IV.

## II. EXPERIMENTAL PROCEDURE

Fourier-transform MIR spectroscopy was used to study the absorption spectra of Zn- and Be-doped Ge. The experimental apparatus consisted of a Bruker IFS 113V Michelson interferometer. The modulated output beam was polarized using a stacked-plate polarizer and then focused onto the sample located in the tail of a Vari-Temp Dewar.[11] The transmitted radiation was filtered and detected by a 1.6 K Ge bolometer[12] located in the same Dewar. The spectra were collected at an apodized resolution of 0.15 $cm^{-1}$.

Samples were cut from low compensation, vacuum-grown Ge containing either $2.3\times10^{14}$ $cm^{-3}$ Be or $2\times10^{15}$ $cm^{-3}$ Zn. The samples, which measured $2\times4\times12$ $mm^3$, were stressed between parallel piston faces with a calibrated force applied through a push rod from outside the cryostat. Thin lead pads were placed between each sample end and piston face in order to

 

guarantee a homogeneous stress. At each stress, pairs of spectra were taken with the MIR electric vector alternately parallel and perpendicular to the stress axis. In addition, these spectra were taken at both 4.2 and 1.8 K in order to reveal temperature effects which can help separate the thermalizing ground-state splittings from the non- thermalizing excited-state splittings. The sample temperature was determined from the vapor pressure of the liquid He in which it was immersed.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows some absorption spectra of Ge:Be taken along the [100] direction at a stress of 11 MPa and at temperatures of 4.2 and 1.8 K. Even at this low stress, the stress-induced splittings dominate the zero-stress Be splittings which result from hole-hole interactions. Figure 2 shows spectra taken under the same conditions in Ge:Zn, but at a slightly lower stress of 10 MPa. The results for Ge:Be were found to be in good agreement with those of Cross *et al.*[13] who recently reported a detailed piezospectroscopic study of Ge:Be. They showed that, at stresses where the small hole-hole interaction can be neglected, the Be double acceptor under uniaxial stress is well described by Kartheuser and Rodriguez's model in which the essentially degenerate $\{\Gamma_8\times\Gamma_8\}$ ground state splits into three components. This stress-induced ground-state splitting is directly reflected in a dramatic temperature dependence of the Ge:Be absorption spectrum as shown in Fig. 1. These temperature effects, resulting from thermalization between the split-ground state levels, were observed in Ge:Be over the *entire* range

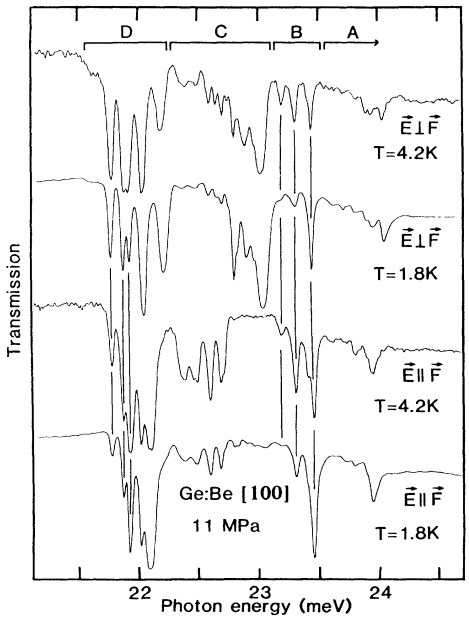


FIG. 1. Representative Ge:Be uniaxial stress spectra taken at a [100] stress of 11 MPa. The spectra depend strongly on both the temperature and polarization. The apodized resolution was 0.02 meV.

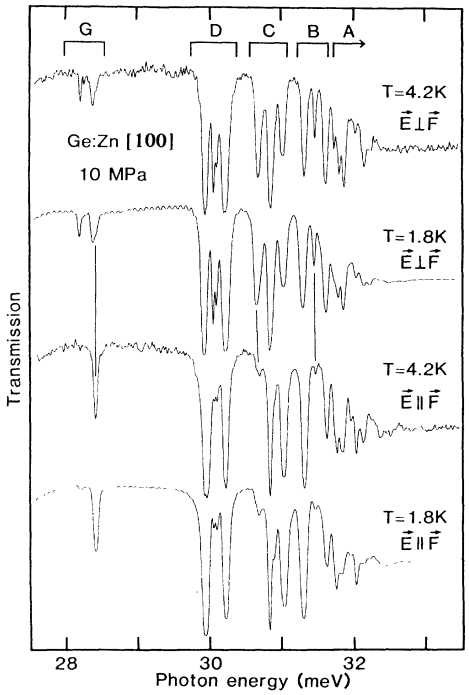


FIG. 2. Representative Ge:Zn uniaxial stress spectra taken at a [100] stress of 10 MPa. In contrast to the Ge:Be results shown in Fig. 1, less fine structure and no temperature effects are observed. In fact, no thermalization was detected over the entire range of [100] stresses studied here. This indicates that all the observed Zn lines originate from a single ground-state level which does not split under [100] stress.

of stress up to 50 MPa. However, for Ge:Zn *no* thermalization could be detected between 4.2 and 1.8 K spectra for *any* stress between zero and 63 MPa. This striking difference in temperature dependence between the Be and Zn results is readily observed by comparing Figs. 1 and 2. Thus Zn, unlike Be, shows no observable stress-induced splitting of the ground state involved in the MIR transitions over the range of stresses studied here. Furthermore, the simplicity of the Zn piezospectra as compared to those of Be again underlines the fact that the ground state involved in the Zn transitions has considerably less degeneracy than the full $\{\Gamma_8\times\Gamma_8\}$.

To reconcile these results, we must first consider that Zn, unlike the Be double acceptor, has at zero stress a large ground-state splitting of $2.4\pm0.1$ meV caused by the hole-hole interaction.[6] Furthermore, at the temperatures used to take these spectra, only the lowest ground-state component is populated, and only this lowest ground-state level is involved in the observed MIR transitions. This immediately suggests that the lowest ground-state level of Ge:Zn is indeed $\Gamma_1$ ($J=0$), since this state cannot be split by stress. Under [100] stress, the $\Gamma_3$ and $\Gamma_5$ ($J=2$) levels of $\{\Gamma_8\times\Gamma_8\}$ split into $\Gamma_1+\Gamma_3$ and $\Gamma_4+\Gamma_5$, respectively. We must, of course, ask ourselves whether these $J=2$ splittings would be large enough to be observed, and to thermalize over the stress range used here, if $J=2$ was instead the lower ground state. Since the

ground-state splitting is known[6] to be 2.4±0.1 meV, and the deformation potential for the Zn ground state should be very close to that of Be, or of that of the single 1S hole in the excited Zn, the size of the expected $J=2$ ground-state splittings can readily be estimated.[14] For example, at a [100] stress of 50 MPa the expected $J=2$ splitting would be ~0.3 meV, while for an equal [111] stress the splitting would be slightly larger. Had they existed, such splittings would have been easily resolvable, and would have shown strong thermalization between 4.2 and 1.8 K.

### A. Piezospectroscopy with F||[111]

Figure 3 shows typical absorption spectra of Ge:Zn with stress applied along the [111] direction. No thermalization was observed between 1.8 and 4.2 K at any stress up to 50 MPa indicating again that the lowest ground-state level does not split with stress. The results of these measurements are summarized in Fig. 4 in which the position and polarization of the various absorption lines are plotted as a function of stress. (A line is considered to be unpolarized if it contains significant elements of both polarization components. In some cases the crossover of two oppositely polarized lines may lead to the appearance of a single unpolarized line.)

Figure 5 shows the energy-level scheme derived from the detailed group theoretical study of Kartheuser and Rodriguez.[9] In our model the ground state is split at zero stress by hole-hole coupling with the lowest state, $\Gamma_1$, 2.4 meV below the higher levels, as already determined.[6] This splitting is large enough to cause complete thermal depopulation of the higher ground states at liquid helium temperatures.

The excited state is represented in the self-consistent-field approximation by the direct product $\Gamma_8\times\Gamma_8'$ where $\Gamma_8'$ is the irreducible representation of the excited single-particle hole state in $\bar{T}_d$ and $\Gamma_8$ that of the hole remaining in the single-particle 1S-like state. In this approximation the $\Gamma_8$-$\Gamma_8'$ hole-hole interaction is ignored, a valid assumption since no splitting of the Zn excited states is observed at zero stress. For stress applied in the [111] direction the symmetry group is reduced from $\bar{T}_d$ to $\bar{C}_{3v}$

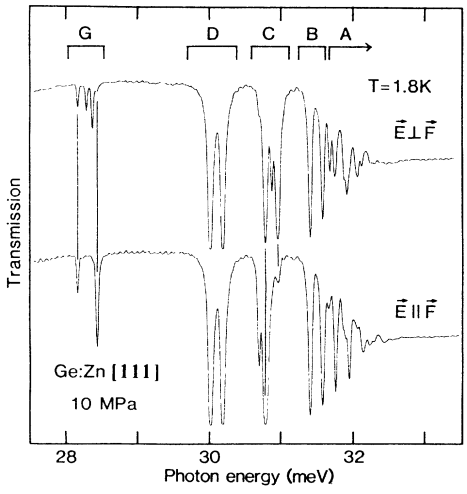


FIG. 3. Representative Ge:Zn uniaxial stress spectra taken at a [111] stress of 10 MPa. Additional data show that no thermalization was observed between 1.8 and 4.2 K, at this or any other [111] stress. The apodized resolution was 0.02 meV.

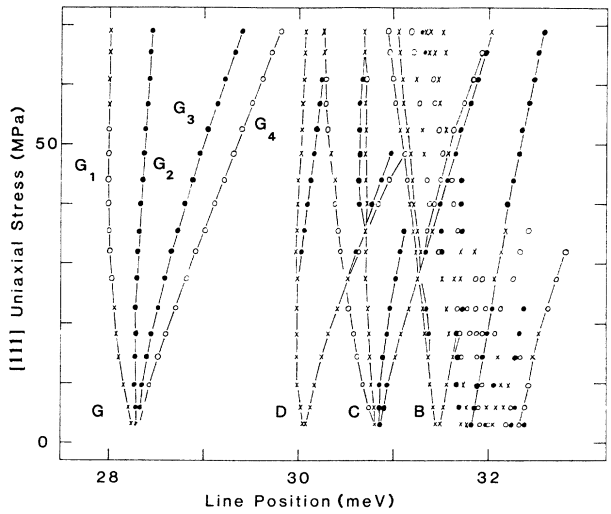


FIG. 4. Stress dependence of the line positions of the *G*, *D*, *C*, *B*, and *A* lines of Ge:Zn for F||[111]. The symbols ●, ○, and × represent E⊥F, E||F, and unpolarized absorption lines, respectively. The lines are drawn for convenience only.

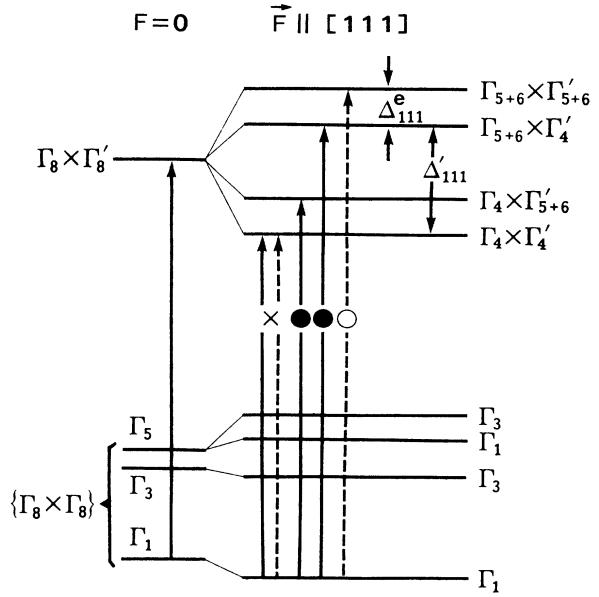


FIG. 5. Energy-level scheme and optical transitions for the [111] stress-induced components of Ge:Zn. The dashed and solid arrows are for E||F and E⊥F, respectively. The figure has been drawn for $d'<0$, $d_e'<0$, and $T<0$. The stress-induced splittings and the associated symbols are defined in the text. The $\{\Gamma_8\times\Gamma_8\}$ ground state is shown to be split by hole-hole coupling into three nondegenerate $\Gamma_1$, $\Gamma_3$, and $\Gamma_5$ levels.

and the $\Gamma_8$ representation splits into $\Gamma_{5+6}$ and $\Gamma_4$ of $\bar{C}_{3v}$ where $\Gamma_{5+6}$ is the Kramers doublet $\Gamma_5+\Gamma_6$. The excited state $\Gamma_8\times\Gamma_8'$ then splits into four levels as shown. These splittings are characterized by $\Delta'_{111}$ and $\Delta^e_{111}$, corresponding to splitting of the single-hole 1$S$-like state and excited hole state, respectively. These coefficients are related to the ground- and excited-state shear deformation-potential constants, $d'$ and $d'_e$ through the following expressions:

$$\Delta'_{111}=\frac{d'S_{44}T}{\sqrt{3}},\quad \Delta^e_{111}=\frac{d'_eS_{44}T}{\sqrt{3}}\ . \tag{2}$$

$S_{44}$ is one of the elastic compliance constants and $T$ is the uniaxial stress, negative for compression.

Comparison between the predicted transitions shown in Fig. 5 and the piezospectroscopic results in Fig. 4 enables us to identify the four $G$ components from their polarization. The $\Gamma_8'$ excited hole state splitting is then given, for example, by the separation of lines $G_3$ and $G_4$, while the splitting between $G_2$ and $G_4$ gives the 1$S$-like $\Gamma_8$ hole state splitting. In the $D$ and $B$ lines, only the 1$S$-like $\Gamma_8$ state splitting is seen at low stress although a small $\Gamma_8'$ splitting becomes apparent at higher stresses. The $C$ line is more complicated because here the excited hole state is represented by the superposition of $3\Gamma_8^-$ and $1\Gamma_7^-$ of $\bar{T}_d$ at zero stress.[13] The two unpolarized components of the $C$ line above 10 MPa are associated with $3\Gamma_8^-$ and display small excited-state splittings at higher stress. The two remaining branches come from the $1\Gamma_7^-$ excited hole state and have no excited-state splitting, since $\Gamma_7$ of $\bar{T}_d$ does not split in $\bar{C}_{3v}$.

The splitting of the single-hole 1$S$-like $\Gamma_8$ state should be virtually unaffected by the state of the excited hole due to the small overlap between the 1$S$-like and excited hole wave functions. This is seen to be the case in Fig. 6 as the single hole $\Gamma_8$ state splittings of the $G$, $D$, $C$, and $B$ lines are observed to agree closely as a function of stress.

The $\Gamma_8$ and $\Gamma_8'$ deformation-potential constants evaluated from the above results are given in Table I and compared with those of various acceptors in Ge.

### B. Piezospectroscopy with F‖[100]

The stress dependence of the Ge:Zn absorption spectrum for the [100] direction is summarized in Fig. 7. A characteristic feature displayed in Fig. 7 is the splitting of the $G$ line into four components where, for stresses above 40 MPa, lines $G_1$ and $G_4$ are unpolarized while $G_2$ and $G_3$ are polarized with E⊥F. This structure is reflected in the $D$ and $B$ lines, except that in the $B$ line the two central components merge into one unresolved line.

The energy-level scheme shown in Fig. 8 was constructed using the same approximations as those employed in Fig. 5. For stress applied along the [100] direction the double group $\bar{T}_d$ reduces to $\bar{D}_{2d}$, and the $\Gamma_8$ representation splits into $\Gamma_6$ and $\Gamma_7$ of $\bar{D}_{2d}$, giving a fourfold splitting of the excited state. The single hole $\Gamma_8$ and $\Gamma_8'$ splittings, $\Delta'_{100}$ and $\Delta^e_{100}$, are related to the shear deformation-potential constants $b'$ and $b'_e$ by

$$\Delta'_{100}=2b'(S_{11}-S_{12})T,\quad \Delta_{100}=2b'_e(S_{11}-S_{12})T\ . \tag{3}$$

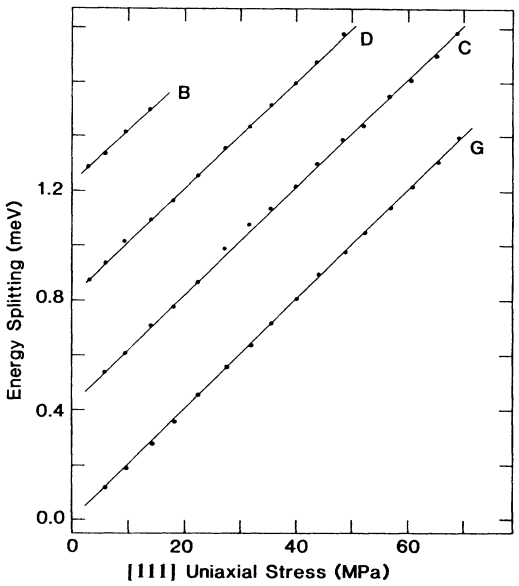


FIG. 6. The splittings of the single hole 1$S$-like states associated with the $G$ ($G_4-G_2$), $D$, $C$, and $B$ lines are plotted as a function of stress in the [111] direction. The data for the $C$, $D$, and $B$ lines have been displaced upwards in energy by 0.4, 0.8, and 1.2 meV, respectively. The solid lines represent linear fits to the data. The slopes are identical to within experimental error.

As can be seen from the set of allowed transitions in Fig. 8, a simultaneous change in sign of $b'$ and $b'_e$ would result in the same ordering of polarized and unpolarized transitions, therefore only the absolute values of $b'$ and $b'_e$ can be determined. The single-hole $\Gamma_8$ and $\Gamma_8'$ splittings can be distinguished from each other by the fact that, as

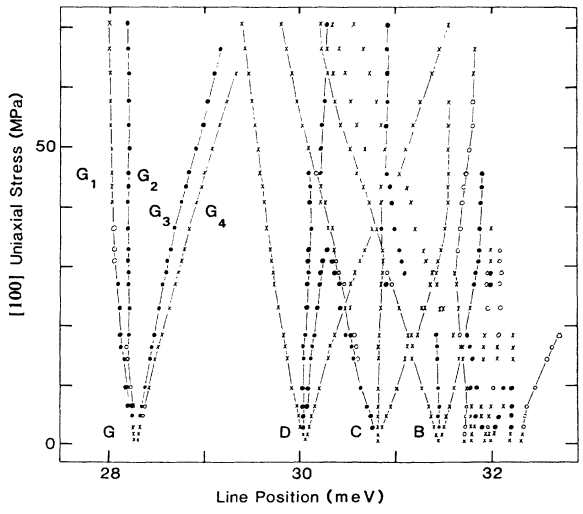


FIG. 7. Stress dependence of the line positions of the $G$, $D$, $C$, $B$, and $A$ lines for F‖[100]. The symbols ●, ○, and × represent E⊥F, E‖F, and unpolarized absorption lines, respectively.

TABLE I. Deformation-potential constants of acceptor states in Ge [eV/(unit strain)].

| | Experiment | | | | | |
|---|---|---|---|---|---|---|
| | Zn[a] | Be[b] | Cu[c] | Zn[d] | Ga[e] | Theory[f] |
| $b'$[g] | ±1.23±0.01 | ±0.93 | 1.300 | −0.75 | −1.33 | −1.26 |
| $d'$[g] | −2.40±0.02 | −4.02 | ~0 | −2.32 | −2.91 | −2.51 |
| $b'_G$ | ±0.38±0.04 | | 0.19 | | 0.213 | 0.44 |
| $d'_G$ | −1.01±0.01 | | −1.00 | −1.45 | −1.10 | 0.88 |
| $b'_D$ | ±0.94±0.03 | ±0.78 | 0.54 | 0.65 | 0.60 | 0.38 |
| $d'_D$ | −0.60±0.02 | −0.22 | ~0 | 0.15 | < \|0.06\| | −0.19 |

[a]Present work.
[b]Reference 13.
[c]Reference 16.
[d]References 10, 17, and 18.
[e]Reference 10.
[f]L. M. Browning, Ph.D. thesis, Purdue University, 1984.
[g]The $b'$ and $d'$ values are those for the $G$ components since level crossing effects are minimal for these states.

for the [111] direction, the $\Gamma_8$ splitting should be approximately the same for all four lines $G$, $D$, $C$, and $B$. This is seen to be the case in Fig. 9, confirming our assignment of the various optical transitions. Unlike the [111] case, the $\Gamma'_8$ excited-state splittings for [100] stress increase for the more weakly bound states, and for the $B$ line becomes equal to the $\Gamma_8$ splitting, causing the merging of the two central lines. This behavior parallels that of the single acceptor Ga in Ge.[10] The shear deformation-potential constants derived from our results agree surprisingly well with those of Ga in Ge as seen in Table I, supporting the single-particle approximation for the excited states.

The assignment of $\Gamma_1$ as the lowest two-hole ground state is amply supported by our results. As can be seen from Figs. 5 and 8, a $\Gamma_5$ ground state should split under stress in either the [111] or [100] direction while the $\Gamma_3$ state would split in the [100] direction only. This splitting would be detected by the presence of extra lines in the absorption spectrum and by thermalization between lines, neither of which was seen in our results. Even if

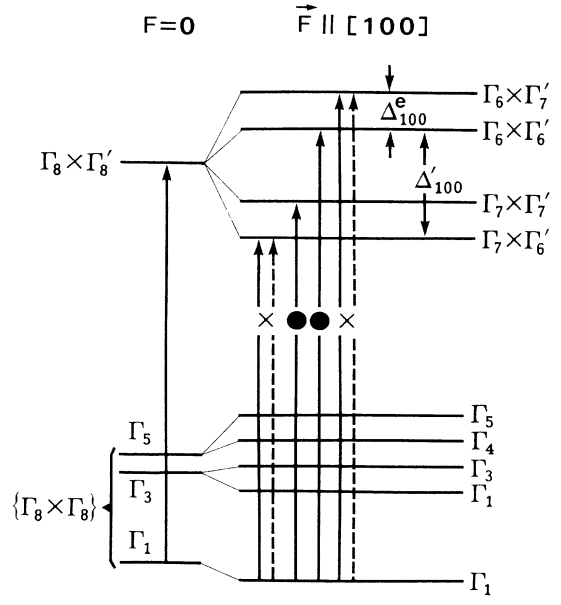


FIG. 8. Energy-level scheme and optical transitions for the [100] stress-induced components of Ge:Zn. The dashed and solid arrows are for $\mathbf{E}\|\mathbf{F}$ and $\mathbf{E}\perp\mathbf{F}$, respectively. The figure has been drawn for $b'<0$, $b'_e>0$, and $T<0$. The stress-induced splittings and the associated symbols are defined in the text. The $\{\Gamma_8\times\Gamma_8\}$ ground state is shown to be split by hole-hole coupling into three nondegenerate $\Gamma_1$, $\Gamma_3$, and $\Gamma_5$ levels.

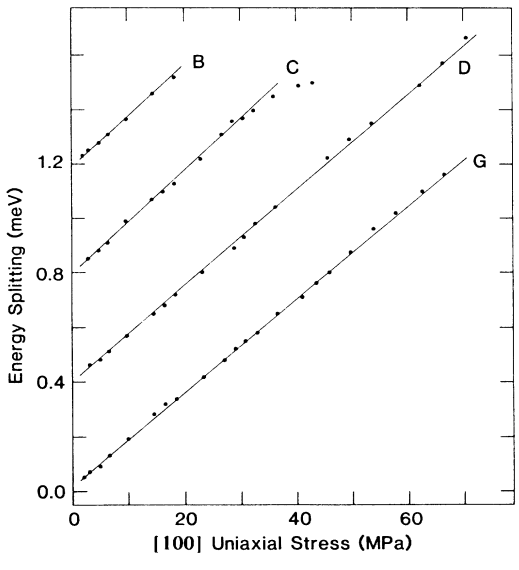


FIG. 9. The splittings of the single-hole ground states associated with the $G$ $(G_4-G_2)$, $D$, $C$, and $B$ lines are plotted as a function of stress in the [100] direction. The data for the $D$, $C$, and $B$ lines have been displaced upwards in energy by 0.4, 0.8, and 1.2 meV, respectively. The solid lines represent linear fits to the data. The slopes are identical to within experimental error.

the stress-induced splitting of these ground states was too small to produce such effects, the polarization selection rules would be different from those shown in Figs. 5 and 8, generally allowing more lines to appear unpolarized. The polarizations observed in our results are completely consistent with a $\Gamma_1$ initial state. On the basis of all of the above evidence, it is clear that the lowest lying level of the hole-hole split ground state of Zn in Ge has $\Gamma_1$ symmetry.

## IV. CONCLUDING REMARKS

### A. Ge:Zn

The model used to interpret the experimental results presented in this paper was based on the group theoretical analysis of Kartheuser and Rodriguez.[9] The hole-hole interaction was fully taken into account for the stress dependence of the ground-state levels. It was shown that the piezospectroscopy of Ge:Zn could only be understood if the $\Gamma_1$ two-hole state is more tightly bound than $\Gamma_3$ or $\Gamma_5$. This conclusion supports our previous assignment of $\Gamma_1$ as the true ground state based on a uniaxial stress study of photoluminescence in Ge:Zn.[6] This "inverted" ground-state ordering is opposite to the ordering which was generally proposed in the literature. There, an analogy with atomic systems and Hund's rule had been used to locate the $\Gamma_3+\Gamma_5$ levels at lower energy than the $\Gamma_1$ level.

For the excited states, the self-consistent-field approximation was utilized to describe their dependence upon uniaxial stresses. The validity of this approximation, in which hole-hole interaction is neglected, was supported by our results, and in particular by the good agreement between the shear deformation-potential constants obtained for Ge:Zn with those of the single acceptor Ge:Ga.

### B. Implications for Ge:Cu triple acceptor

Recently, Salib *et al.*[15,16] investigated the piezospectroscopy of the neutral triple acceptor Cu in Ge. In their analysis, the zero-stress ground state was given by $\{\Gamma_8\times\Gamma_8\times\Gamma_8\}\equiv\Gamma_8$ and the excited states by $\{\Gamma_8\times\Gamma_8\}\times\Gamma_n'$ $(n=6,7,8)$. The $\{\Gamma_8\times\Gamma_8\}$ states of the two holes left in the $1S$-like ground-state configuration were taken to be degenerate in the absence of stress. This degeneracy assumption leads to a complicated model for the stress splitting of the excited states, with $\{\Gamma_8\times\Gamma_8\}\times\Gamma_8'$ splitting into at least six components. Coupled with the twofold stress splitting of the $\Gamma_8$ ground state, there is clearly considerable room for complexity in the piezospectroscopy of neutral Cu in such a model.

Surprisingly, the observed splittings were of a very simple nature and remarkably similar to those of single acceptors in Ge.[15,16] The observed splitting patterns were explained within the framework of the above model by postulating the stress splitting of the $\{\Gamma_8\times\Gamma_8\times\Gamma_8\}\equiv\Gamma_8$ ground state to be identical to that of the two holes in the $\{\Gamma_8\times\Gamma_8\}$ state associated with the final state. Although the pattern of the splittings could be reproduced under this assumption, problems remained with the intensities of the lines, and in particular, with the temperature dependences of the relative intensities.[15,16]

We wish to propose an alternate explanation of the surprisingly simple piezospectroscopy of the neutral Cu triple acceptor which follows from the fact that the $\{\Gamma_8\times\Gamma_8\}$ state of the two $1S$-like holes in excited Cu might well be split by the same hole-hole interaction considered here for double acceptors. In this model, the $\{\Gamma_8\times\Gamma_8\}$ two-hole state of the excited triple acceptor is taken to have a *large* zero-stress hole-hole splitting into $\Gamma_1$, $\Gamma_3$, and $\Gamma_5$ states, with $\Gamma_1$ lowest in energy. The observed transitions are then not $\Gamma_8\rightarrow\{\Gamma_8\times\Gamma_8\}\times\Gamma_n'$ but rather $\Gamma_8\rightarrow\Gamma_1\times\Gamma_n'\equiv\Gamma_n'$, and an explanation for similarity with the single-acceptor results is immediately obvious.

These two models predict quite different behaviors for the thermalization of the intensities of the stress-split components. In the model of Salib *et al.*,[15,16] all four observed components of a transition to a $\Gamma_8'$ excited state contain contributions from *both* levels of the stress-split initial state. Thus all four components should remain with constant relative intensity in the low-temperature limit ($kT\ll$ the ground-state splitting). In our model, the four components are interpreted as transitions from a twofold-split initial state to a twofold-split final state (as in the single-acceptor case). We would therefore predict that two of the four absorption lines should completely vanish in the low-temperature limit. While Salib *et al.*[16] have reported some preliminary thermalization data, it does not cover a sufficient range to distinguish between the two models.

Given what has been learned of the hole-hole splitting in double acceptors, it does not seem unlikely that this splitting for the two holes left in the $1S$-like states of the excited triple acceptor could be quite large. The size of the splitting is strongly dependent upon the degree of localization of the holes involved, and this could be large for two $1S$-like holes bound to the triply charged Cu ion, since the excited $p$-like third hole will have negligible amplitude in the central-cell region.

If our proposed model is correct, it should have consequences for the unperturbed Cu absorption spectrum as well. One would expect to observe transitions to $\Gamma_3\times\Gamma_n'$ and $\Gamma_5\times\Gamma_n'$ excited states (here $\Gamma_3$ and $\Gamma_5$ are two-hole states obtained from $\{\Gamma_8\times\Gamma_8\}$). It is also, of course, possible that the two-hole $1S$-like $\{\Gamma_8\times\Gamma_8\}$ state for excited neutral Cu is split but then the $\Gamma_1$ state does not lie lowest in energy, although this should result in a more complicated piezospectrum. Further experimental studies of the spectroscopy of neutral Cu in Ge, both with and without external stress, would clearly be desirable.

## ACKNOWLEDGMENTS

We wish to thank A. K. Ramdas for the loan of a polyethelene stacked-plate polarizer. This work was supported by the Natural Sciences and Engineering Research Council of Canada, and two of the authors (D.L. and I.J.B.) would like to acknowledge the support of the Council.

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