

Evidence for As lattice location and Ge bound exciton luminescence in ZnO implanted with ^{73}As and ^{73}Ge

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The results of photoluminescence (PL) measurements performed on high quality single crystal ZnO implanted with radioactive ^{73}Ga and ^{73}As , both of which decay to stable ^{73}Ge , are presented. Identical effects are observed in the two cases, with a sharp line at 3.3225(5) eV found to grow in intensity in accordance with the growth rate of the Ge daughter atom populations. On the strength of the well-established result that Ga occupies Zn sites, we conclude from the identical outcomes for ^{73}Ga and ^{73}As implantations that implanted As also preferentially occupies Zn sites. This result supports the findings of others that As preferentially occupies the Zn rather than the O site in ZnO. The thermal quenching energy of the 3.3225(5) eV line is found to be only 2.9(1) meV in contrast to its large spectral shift of 53.4(1) meV with respect to the lowest energy free exciton. The PL is attributed to exciton recombination at neutral Ge double donors on Zn sites involving transitions that leave the donor in an excited state.

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I. INTRODUCTION

The potential of ZnO for short-wavelength optoelectronic device applications and the challenges and obstacles impeding that aim are well documented in the literature.^{1–3} The matter of controlled doping, especially for the production of *p*-type material, is a particular challenge, and extensive research has been carried out toward that end for many years.^{4,5} Recent theoretical work has re-examined some likely candidate *p*-type impurities such as N and cast doubts on its efficacy,⁶ as it appears to be an extremely deep acceptor with an ionization energy of 1.3 eV. Other potential *p*-type impurities such as As have also been proposed, and *p*-type conductivity has been reported by various groups, but as yet, a commercially viable *p*-type doping recipe has not been reported.^{2,7} In the case of As, these impurities—if occupying the O site in the lattice—are predicted to also form deep acceptors,⁸ but the electron emission channeling work of Wahl *et al.*⁹ has shown that, contrary to expectation, the preferred location for As is the Zn site, a result that accounts for the failure of As to act as a simple substitutional acceptor and *p*-type dopant in ZnO.

Consequently, there has been further theoretical work devoted to taking a broader view of the doping behavior of a variety of impurities, not just those with potential *p*-type character. Such work has included the group-IV impurities Si and Ge, both of which are predicted to behave as double donors when located on Zn sites in the ZnO crystal.¹⁰ In this work we report the results of photoluminescence (PL) measurements on ZnO samples implanted with radioactive ^{73}As and ^{73}Ga impurities, both of which have ^{73}Ge as the final stable product of the decay. We find the same behavior in both cases—both As and Ga occupy Zn sites—and we present experimental reports of double donor bound exciton luminescence in high quality single crystal ZnO.

II. EXPERIMENT

Nominally undoped high quality single crystal ZnO obtained from Tokyo Denpa Ltd. (Tokyo, Japan) and Rubicon Technology, Inc. (Illinois, USA) was used. Radioactive ion implantation was performed at the ISOLDE facility at CERN using an implantation energy of 60 keV and typical doses of 5×10^{12} atoms cm^{-2} . ^{73}Ga isotopes were provided by proton activation of a UC target with subsequent laser ionization and mass separation; ^{73}As was provided by the combination of a ZrO target and plasma ion source. Beam purities for Ga were greater than 95%; γ -ray spectra for the implanted isotope revealed no significant isobaric contamination. For ^{73}As , it was necessary to wait until short-lived isobars such as ^{73}Se had decayed before proceeding with any thermal treatments.

After implantation each sample was annealed at 1073 K for 30 min in vacuum to remove implantation damage. Following annealing, the samples were transferred to either a liquid-He flow or a Janis closed cycle cryostat for low-temperature PL measurements. Luminescence was generated by the 325-nm line of a HeCd laser operating at 80 mW. All spectra were recorded at either 1.6 K (^{73}Ga) or 4 K (^{73}As). The luminescence was analyzed by a SPEX 0.75 m grating spectrometer equipped with a LN₂-cooled Jobin-Yvon charge-coupled device detector. PL spectra were collected over a period of about five half-lives following annealing of the implanted sample. The spatial reproducibility of the beam spot location on the sample was within $\sim 100 \mu\text{m}$. Control samples subjected to the same annealing treatment did not produce the new luminescence observed for the implanted samples.

III. RESULTS

The PL emission spectrum of Tokyo Denpa ZnO for both unimplanted material (a) and material implanted with ^{73}As (b) is shown in Fig. 1. It can be seen from the figure that the band-edge region around 3.35–3.37 eV is dominated by

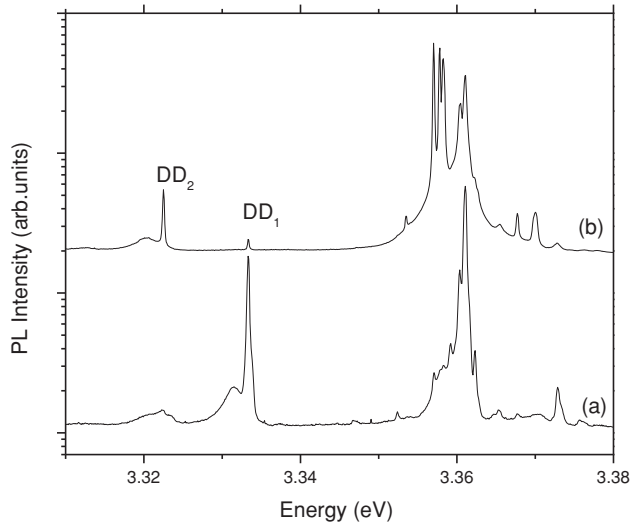


FIG. 1. Representative spectra of Tokyo Denpa ZnO: (a) unimplanted Tokyo Denpa Ltd. ZnO, and (b) ^{73}As implanted ZnO after most of the ^{73}As has decayed to ^{73}Ge .

the well-known I_n lines which are due to ionized and neutral single donor bound exciton recombination, commonly labeled DBX.¹¹ The origin of the line at 3.333 eV, which was labeled as DD by Schildknecht *et al.*¹² and DD_1 in our earlier work,¹³ remains uncertain, although Meyer *et al.*¹¹ conclude that it is due to excitons bound at structural defects. The DD_1 line does not change significantly in intensity over time, so we therefore normalize all intensity values to this feature in subsequent calculations. In the spectra of control (unimplanted) samples, the relative intensities of the various I_n lines, and of DD_1 in comparison to the I_n lines, change upon annealing, as we find in implanted samples. However, since the focus of this study is on the lines in the region 3.32–3.34 eV, no further comment will be made on the I_n line spectra other than to note that no changes were observed that could be associated with the half-life of implanted atoms. Likewise, we do not repeat our analysis of the dependence of I_8 and I_1 on the Ga population, which is described in detail in our earlier work where a firm identification of I_8 and I_1 with Ga was made.¹³ Regarding the spectral range below 3.2 eV, the control samples (both as-received and vacuum annealed) produce broad largely unstructured bands across the visible range. Although a structured band is observed in the Ga- and As-implanted samples following annealing, there are no systematic variations in the band intensity that correlate with the half-life values of the implanted ions.

Figure 1(b) shows the spectrum of a ZnO sample following the decay of implanted $^{73}\text{As} \rightarrow ^{73}\text{Ge}$. In the region 3.32–3.34 eV, in comparison to the unimplanted sample, we see the appearance of a new feature which we label DD_2 , and which is completely absent in the unimplanted sample. The position of this line is 3.3225(5) eV with a half-width of ~ 0.3 meV. DD_2 overlaps with a broad line centered at 3.3220 eV, but this broad line is not directly related to DD_2 as their relative intensity varies over time. The DD_2 line is also observed for the case of radioactive ^{73}Ga implantations, with a greater linewidth of ~ 0.9 meV, which we attribute to the poorer quality of the ZnO crystal used in that instance (sample from Rubicon

Technology Inc). The implication of this finding, that radioactive As and Ga implantations both result in the same final stable defect center, is discussed below. The spectral shift of DD_2 compared to the FX_A free exciton is 53.4(1) meV.

The changes that take place in the PL spectra over time following implantation and annealing are presented in Fig. 2, which shows how the intensity of DD_2 changes as the mother isotopes (^{73}As or ^{73}Ga) decay to the final stable product ^{73}Ge . As noted above, the intensity values for these spectra are all normalized to the intensity of DD_1 .

From the normalized spectra, clear growth of the luminescence feature DD_2 at 3.3225 eV can be seen in both samples over the period of the measurements. Fits to the data show that the growth of the DD_2 intensity corresponds in each case to the growth of the daughter population following the decay of the implanted mother isotope. For the case of ^{73}Ga the fit to the half-life is found to be 4.9 ± 0.2 h while for ^{73}As it is found to be 78.3 ± 3.1 d, both of which agree—within the fit uncertainty—to the tabulated radioactive half-life values of 4.76 h and 80.3 d, respectively.¹⁴ We conclude therefore that the DD_2 luminescence is due to Ge impurities produced from the decay of the implanted ^{73}As and ^{73}Ga .

To gain more information about the nature of this luminescence we investigated the dependence of the DD_2 line intensity on temperature over the range from ~ 3 K to roughly 20 K, by which temperature the line was no longer detectable. Comparative spectra demonstrating the temperature dependence of both the DD_2 and DD_1 lines, and including the I_{10} line, are shown in Fig. 3(a). I_{10} is included in Fig. 3 to demonstrate the difference in behavior of DD_2 in comparison to the I_n lines—it is clear that the intensity of DD_2 decreases quite sharply with increasing temperature when compared to both DD_1 and I_{10} .

From the intensity values obtained as a function of temperature, the thermal quenching energy ΔE for DD_2 was calculated using the standard equation, where the quantity below is plotted versus $1/T$. The notation $DD_2(T)$ denotes the intensity of the DD_2 line as a function of temperature:

$$\ln \left\{ \left(\frac{DD_2(0)}{DD_2(T)} - 1 \right) \left(\frac{1}{T^{3/2}} \right) \right\} = \ln(g) - \Delta E/kT,$$

where g is the density of band states relative to the density of DD_2 initial exciton states. The slope of a linear fit to the data using this equation gives a value for the thermal quenching energy of 2.9 ± 0.1 meV, a relatively low value when compared to some of the other DBX binding energies in ZnO and much less than the spectral shift with respect to FX_A of 53.4 ± 0.1 meV. For example, a value of ~ 22 meV was found for the thermal quenching energy of I_9 in this work, close to the value obtained previously by others¹¹ and close to the 19.2-meV spectral shift of I_9 from the FX_A free exciton.

IV. DISCUSSION

A. Radioactive decay recoil and implantation-induced defects

In analyzing data originating from the radioactive decay of implanted isotopes it is important to consider the likelihood of defects being created as a result of recoil. For example, in the work of Weyer *et al.*,¹⁵ where the Mossbauer probe ^{57}Fe

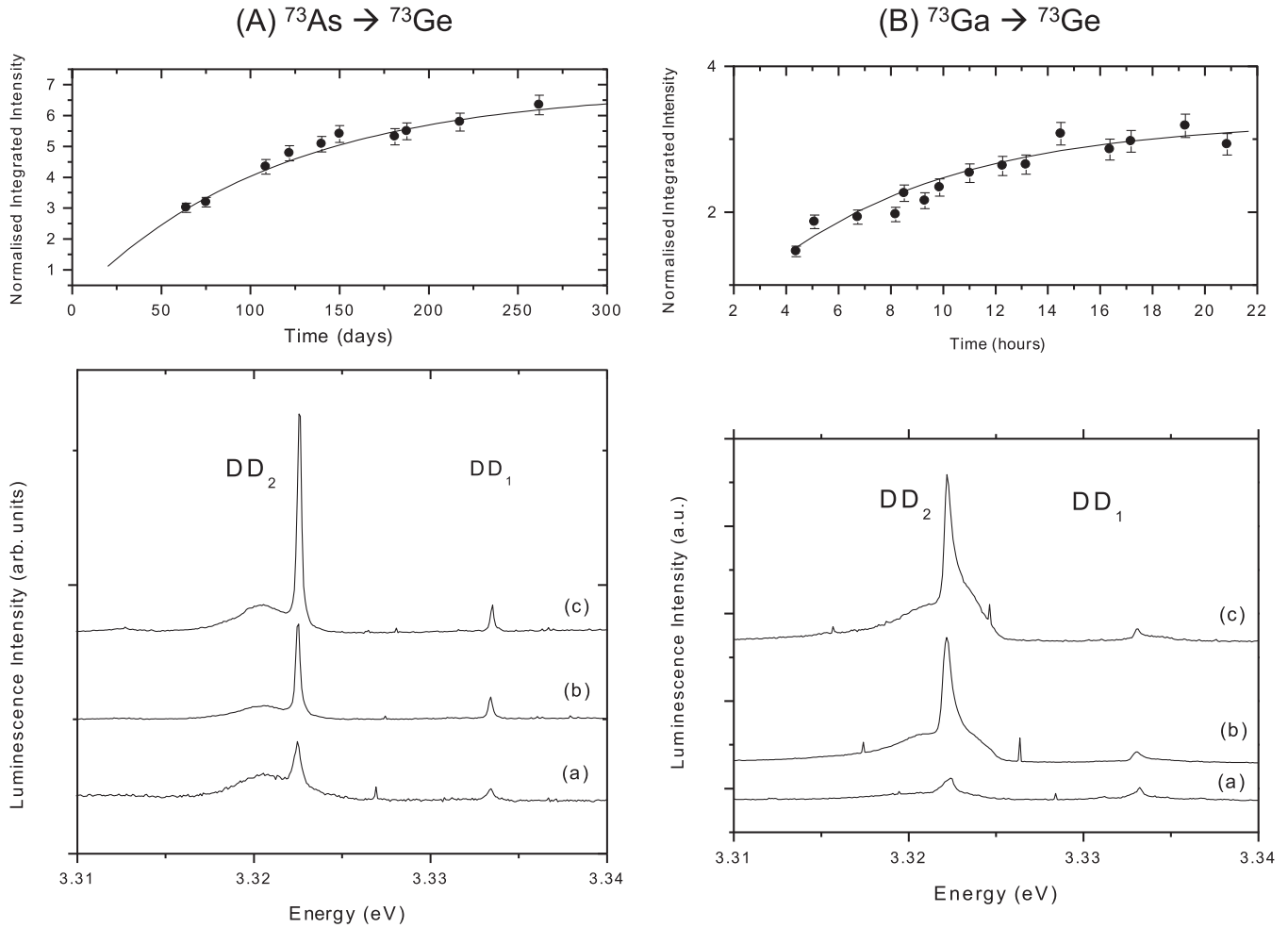


FIG. 2. Representative spectra depicting the growth of the line DD_2 following implantation of ^{73}As (A) and ^{73}Ga (B). Fits to the exponential growth of the DD_2 intensity are also included. The three spectra in each case show the evolution of the growth of DD_2 over the span of five half-lives, (a) being soon after implantation and (c) being close to the end of five half-lives.

was used to study the magnetic properties of ZnO, the beta decay of the mother isotope ^{57}Mn , for which the average recoil is ~ 40 eV¹⁶ resulted in the production of Zn interstitials. In our studies, ^{73}As decays to ^{73}Ge via electron capture and ^{73}Ga decays to ^{73}Ge via β^- emission with average recoil energies of only ~ 1 eV and 10 eV, respectively. In both cases, this is insufficient to dislodge a host atom from a substitutional position in the lattice, for which the threshold values are typically 57 eV for O and between 18.5 and 57 eV for Zn.^{17,18} In earlier work we found that evidence of defect formation is present in the PL spectrum only where the recoil energy is high.¹³ Given the low recoil energies in the present cases, and the absence of any evidence of defect formation in the PL spectra, we exclude consideration of recoil-induced defects in this study.

Regarding defect generation due to ion implantation, the evidence from our studies is that annealing at temperatures of 750 °C and above results in a marked improvement in the PL efficiency. However, it is not guaranteed that all implanted atoms are located in a perfect crystalline environment following annealing. For example, Wahl *et al.*⁹ note that approximately 30% of implanted As occupy sites other than the Zn site after annealing in vacuum at 800 °C. Consequently, there remains the possibility that a minority of the implanted As is

located at structural defects following annealing, and the same would hold for a corresponding minority of the daughter Ge atoms also. However, there are no reports in the literature, to our knowledge, of configurations for Ga in ZnO other than the simple substitutional impurity Ga_{Zn} .

B. Location of Ga and As impurities in ZnO

We ground our discussion on the well-established behavior of Ga impurities in ZnO. Ga is a common donor impurity, with diffusion and ion implantation of Ga both leading to the characteristic DBX line I_8 in the luminescence spectrum.^{19–22} Our first study of ZnO:Ga using radioactive isotopes of ^{72}Zn and ^{73}Ga confirmed those well-established results,¹³ and the stable Ge impurities produced from the decay of implanted Ga undoubtedly occupy Zn sites predominantly, based on the discussion in Sec. IV A above.

The case of As impurities in ZnO has a rich recent literature—see, for example, Refs. 9, 23, and 24, and references therein. This has been generated by the possibility of As_O producing p -type material where As substitutes for O.²⁵ The hoped-for success of As_O as a simple p -type dopant has not materialized, and instead a complex defect of an As atom and

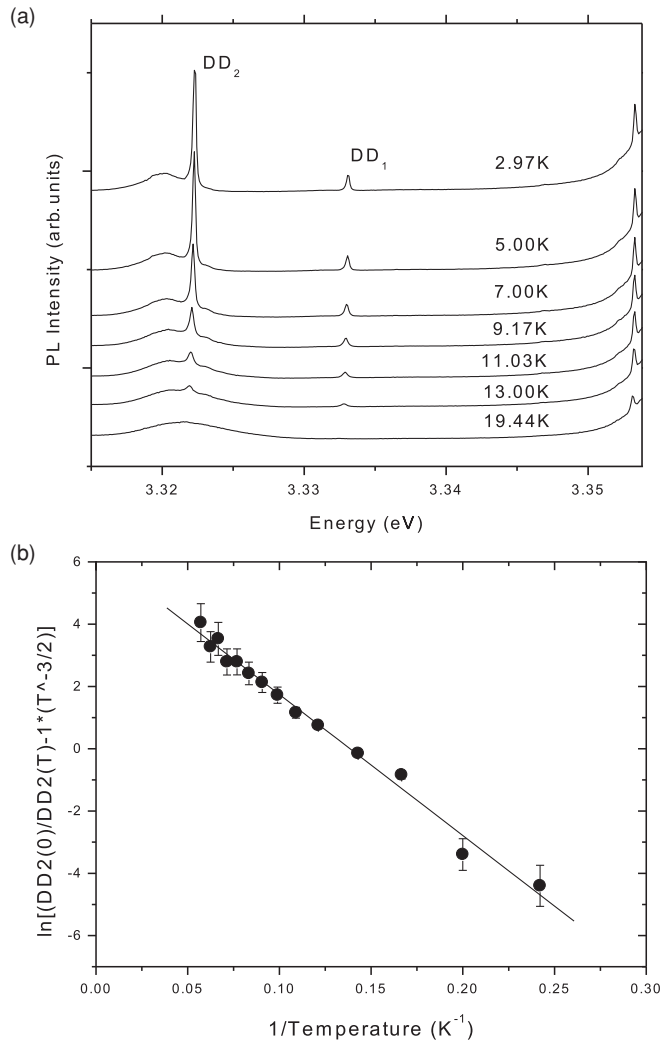


FIG. 3. (a) PL spectra at various temperatures for ZnO:As/Ge, and (b) log plot of the DD_2 line intensity compared to its low-temperature value plotted against inverse temperature. See text for details of the fitting function.

two Zn vacancies ($As-2V_{Zn}$) has been proposed as the source of observed acceptor doping.²⁶ Experimental evidence for the preferred location of As impurities in ZnO would clearly be very useful to illuminate this point. As noted above, such evidence has been reported by Wahl *et al.*⁹ from electron emission channeling studies where they conclude that the Zn site is clearly preferred, with only a few percent (if any) of the implanted As being on the O site. Our PL measurements on ZnO doped with radioactive As in this study are also directed at determining the preferred location of As impurities. As we have reported above, we find the same outcome for ^{73}As and ^{73}Ga implantations, both of which decay to ^{73}Ge . Since both cases result in the same new line (DD_2) in the PL spectrum and since it is known that ^{73}Ga occupies the Zn site, we conclude that As atoms implanted in ZnO occupy the same site as implanted Ga, *i.e.*, As favors the Zn rather than the O site. Taken together, the emission channeling and PL measurements provide strong evidence that As favors the Zn site in ZnO and they support the view that group-V impurities generally do not act as simple O-site acceptors in ZnO. This in turn has important

consequences for various proposed p -type doping strategies for ZnO and points to the necessity for critical re-assessment of the reported p -type behavior in As-doped materials, as reported in Ref. 26. We note also that our results are consistent with the theoretical work of Lyons *et al.*¹⁰ who showed that the formation energy of Ge on a Zn site is lower than that for an O site.

C. Nature of the Ge-related luminescence in ZnO

There have been previous reports of Ge-related luminescence in ZnO. In the case of Kim *et al.*²⁷ samples were grown by mixing GeO with ZnO in the source material, the GeO concentrations used were in the range 0.2–1 mol %, and the samples were mixtures of ZnO and GeO rather than ZnO crystals with a dilute concentration of Ge impurities. As the samples used in this study involve low dose implantations, there are orders of magnitude differences in the impurity concentrations. We note, however, that the broad Ge-related line reported at 3.324 eV by Kim *et al.*²⁷ and attributed to GeO color centers in Ge suboxides in the crystals lies at approximately the same position as the broad line under DD_2 in our study, raising the possibility that the latter may be due to GeO complexes produced in our samples. Such complexes would involve multiple Ge atoms and the characteristic half-life dependence on time, which applies to isolated atoms only, would not be expected for luminescence due to such complexes. In other studies of Ge in ZnO, PL lines are also attributed to color centers in GeO rather than to isolated Ge impurities in ZnO.^{28–30} We are satisfied that none of these earlier works included luminescence attributable to isolated Ge impurities.

The most notable features of the DD_2 line are its sharpness [full width at half maximum only 0.44(1) meV] and its low thermal quenching energy [only 2.9(1) meV] relative to its spectral position at ~ 53.4 meV below the FX_A free exciton. Some PL features at the approximate position of DD_2 have been attributed to free-to-bound (or specifically electron-to-acceptor) transitions where a free donor electron recombines with a hole,¹² or to two-electron satellite lines (TES) of donor bound excitons.¹¹ We will consider the former attribution first and will return to the matter of TES lines below. Free-to-bound features are characteristically broad, and their intensity relative to other shallow luminescence features such as bound excitons tends to increase with increasing temperature. For DD_2 , neither of these attributes applies. In particular, the loss of intensity with increasing temperature is very marked, as noted above. The sharpness of the line points to DD_2 being due to transitions between bound states, and the position (within one LO phonon energy of the free exciton) to excitonic recombination. Given that the line is clearly associated with Ge impurities, and that the Ge impurities occupy Zn sites, we therefore attribute the DD_2 luminescence to bound exciton recombination at Ge_{Zn} impurities. In that configuration, a neutral Ge atom will act as a double donor, having two electrons in excess of local bonding requirements, and so we attribute the DD_2 line to bound exciton recombination at Ge_{Zn} double donor impurities. This attribution is supported by the very small thermal quenching energy of 2.9 meV, which is consistent with weak binding of the exciton at a double donor, *i.e.*, an impurity with a completely full (and in analogy to the He atom, chemically inert) 1S shell.

The large difference between the 53.4-meV spectroscopic energy shift of DD_2 from the FX_A position and its low thermal quenching energy of only ~ 2.9 meV can be accounted for if the “bare” Ge double donor is left in an excited state following exciton recombination. There are two situations where such an outcome can arise. A bound exciton radiative process leaving the bare double donor defect in an excited state can be discussed either in terms of a TES process, where a nonrecombining “spectator” electron is excited into a higher state of the defect,³¹ or in terms of transitions from the double donor bound exciton system (consisting of three electrons and a hole bound at the donor site), where one of the electrons occupies a shallow donor excited state before the recombination takes place.³² In either case, the PL line is shifted downwards by the energy difference between the donor ground state and the excited state involved.^{31,32} In the present study, the available data for DD_2 are not sufficient to allow us to distinguish between these alternatives.

Our provisional conclusion concerning the nature of the DD_2 line is that it is due to bound exciton recombination at a Ge double donor leaving the neutral Ge donor core in an excited state. This identification can account simultaneously for the small thermal quenching energy and the large spectroscopic energy shift of the line with respect to the free exciton energy. Although Ge atoms located at implantation-induced defects cannot be totally ruled out as the origin of the PL, the most logical interpretation is that the dominant impurity center for all cases studied, Ge_{Zn} , is the source of the PL. The precise nature of the double donor bound exciton complex, its energy-level structure, and the selection rules governing its PL transitions remain to be determined. A more detailed study of this system using molecular or molecular ion models of the type introduced by Hopfield³³ or in terms of the shell model³² may assist us in understanding the details of the various recombination channel probabilities and their relevance to the present case. Further confirmation of this provisional

assignment by means of Zeeman spectroscopy and a study of the other group-IV impurities in ZnO would also be desirable. In particular, ZnO:Si, which is predicted to have properties very similar to ZnO:Ge,¹⁰ should provide an excellent case for detailed comparison.

V. CONCLUSIONS

We have examined the photoluminescence of ZnO crystals implanted with radioactive ^{73}Ga and ^{73}As , both of which decay to stable ^{73}Ge . Implanted ^{73}As is found to lead to the same end result in the PL spectrum as implanted ^{73}Ga , indicating the As impurities substitute for Zn as occurs for Ga impurities. Our results support the finding of Wahl *et al.*⁹ from electron emission channeling experiments that implanted As favors the Zn site in ZnO, and they provide further support for the view that group-V impurities generally do not act as simple O-site acceptors in ZnO, which has potentially important consequences for proposed p -type doping options in ZnO.

A new line observed in the PL spectrum at 3.3225(5) eV grows in intensity in correspondence with the half-life of ^{73}Ga and ^{73}As atoms decaying to ^{73}Ge . The thermal quenching energy of the line is only ~ 2.9 meV whereas the spectral binding energy with respect to the FX_A free exciton is ~ 53.4 meV. The observed line is attributed to exciton recombination at neutral Ge double donors, where weak exciton binding (due to the inert nature of the filled $1S$ shell of the bare double donor) accounts for the small value of the thermal quenching energy, and where the recombination leaves the donor in an excited state, thereby accounting for the large spectral binding energy.

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