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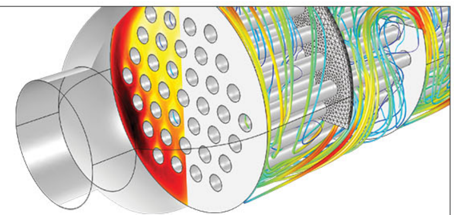

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Optical properties of donor-triad cluster in GaAs and GaN

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The effect of the transition energy of three-donor clusters on far infrared absorption in n-type semiconductor materials has been investigated by a multiconfigurational self-consistent-field model calculation and applied to GaAs and GaN systems. We show that it is crucial to consider the many-particle correlation effects within three-donor clusters. With electron correlation taken into account, the present results support the interpretation of a very recent unidentified peak energy observed in absorption measurement of GaN as due to electronic transitions in these clusters. We also corroborate the suggestion that the X line in GaAs arises from such transitions. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1515121]

In a lightly n-type doped semiconductor, low-temperature spectroscopic measurements exhibit a series of atomic like lines which correspond to the optical transitions of isolated impurity atoms. As the impurity concentration increases donor clusters rapidly become important. As the clusters get more dense the absorption edge drops since one would expect that clusters with larger numbers of donors will absorb at low energies, below the ionization and transition levels of the isolated impurities.[1–3] Bajaj *et al.*[1] have observed a peak on the low energy side of the $1s$ to $2p$ transition, denoted as line X, in their spectroscopic investigations of donors in three different III–V and II–VI semiconductor systems.

The investigation of shallow donors in GaN-based wide band gap semiconductors has recently attracted much interest as an important issue in the fabrication of optoelectronic and electronic devices. Work to date has concentrated on the search for optical transitions of these donor impurities.[4–8] In recent Fourier transformed infrared measurements of n-type doped wurtzite GaN by Moore *et al.*[8] an unidentified sharp absorption line on the low energy side of the $1s$ to $2p$ transition was obtained at a certain impurity concentration. However, an explanation to the origin of this line was not provided. Since the position of the line is rather stringent, it cannot be explained in terms of transitions between isolated impurities. The first attempts to explain such low energies were carried out by Nagasaka and Narita,[9] who adopted the Heitler–London approximation, and by Golka and Piela,[10] who used a version of the Hartree–Fock procedure adapted to a donor-triad cluster.[3] Canuto and Ferreira da Silva[2] calculated the dielectric function of the triad molecule using the *ab initio* self-consistent field (SCF), or Hartree–Fock, and the second-order Møller–Plesset levels of theory,[11–13] and they found anomalies in the dispersion. These authors have suggested that such donor-molecular configurations may be responsible for structureless photoconductivity and absorption tails observed at energies lower than the isolated donor energy, but they all failed to obtain reliable results.

With these investigations in mind, we have aimed the present work at investigating the X line in n-type GaAs as well as the low energy peak in n-type hexagonal GaN. The electronic structure of the donor clusters is likely to be strongly affected by electron correlation, and self-consistent field calculation is inadequate even to capture the qualitative characteristics of the absorption for relatively separated molecular configurations. In this letter, we have therefore pursued the investigation along the lines of a donor-triad-cluster model, but instead employed a multiconfigurational self-consistent field approach to electronic structure determination. We show that by the proper inclusion of electron correlation, the sharp absorption line X in GaAs as well as in GaN can be explained as electronic $H_3 \rightarrow H_3^+$ transitions in three-donor molecules.

In our model, the ionization energy from the H_3 transi-

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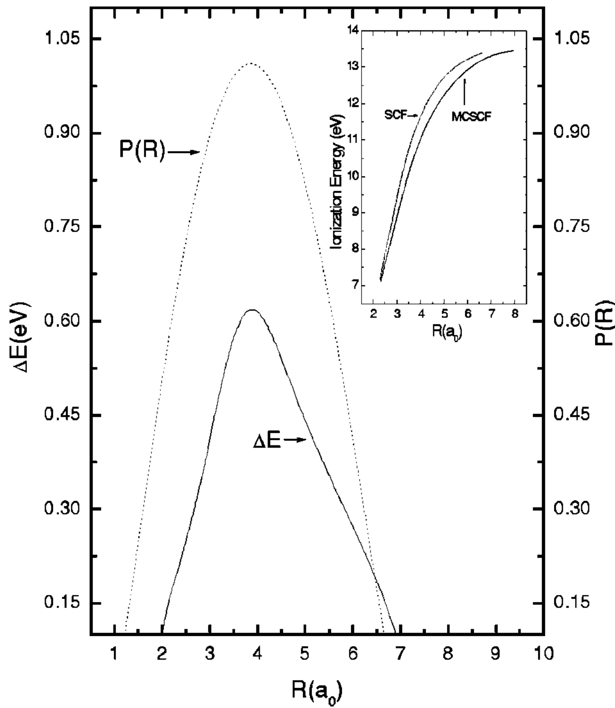

FIG. 1. Difference $\Delta E = E_{\mathrm{SCF}} - E_{\mathrm{MCSCF}}$ in ionization energies as a function of interatomic distance R. $P(R)$ is the distribution function of the three-donor molecule.

tion corresponds to the energy required to promote an electron from the three-donor molecule to the bottom of the conduction band. All calculations of the ionization potential of H_3 were performed at the *ab initio* multiconfigurational self-consistent-field (MCSCF) level.[14] Employing complete active space (CAS) reference states, the N-particle space is determined by all possible excitations within the active space, whereas orbitals in the inactive space are kept double occupied and those in the secondary space are kept unoccupied. In the case of H_3, the natural choice is an active space consisting of three electrons in three orbitals in order to allow the complex to dissociate into three separate hydrogen atoms. This gives a total variational space of eight spin-adapted configurations and a ground state of doublet spin symmetry 1^2A. For the cation H_3^+, the singlet ground state 1^1A was optimized with an identical CAS, thus including six spin-adapted configurations. A standard, high-quality, augmented, correlation consistent, triple-zeta basis set given by Dunning[15] was employed, and we have used spherical-harmonic like basis functions. Since a multideterminant description of the wave function is imperative in order to break chemical bonds, we expect the present ionization potential to be significantly improved for configurations with large interatomic distances.

In Fig. 1, we show the difference between ionizations energies for triangular configurations determined at the electron uncorrelated SCF (Ref. 2) and the electron correlated MCSCF levels, respectively. Within the limit of separation the *exact* ionization energy obviously equals that of the hydrogen atom. From Fig. 1 it is also clear that the SCF results suffer large discrepancies in interatomic separation above $2a_0$. As we have pointed out, it is only in the MCSCF approach that the three hydrogens dissociate correctly into

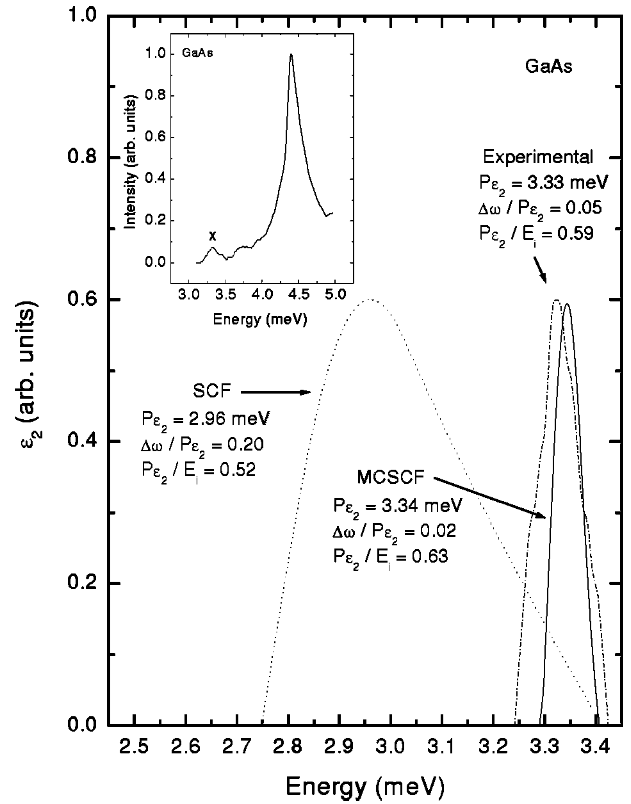

FIG. 2. Imaginary part of the dielectric function for line X in n-type GaAs. The inset shows the results of Bajaj *et al.* (Ref. 1).

three separate neutral atoms, and thus, beyond $4a_0$ the SCF results are not reliable at all.

For doped semiconductors, we only need a change of units. The effective Bohr radius $a_0^* = a_0/(E_i^* \epsilon)$ is obtained from the experimental values of the ionization energy E_i^* and the low-frequency dielectric constant of the semiconductor: $\epsilon(\mathrm{GaAs}) = 12.4$ and $\epsilon(\mathrm{GaN}) = 10.0$.

The dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ describes the optical response of the material, and it is directly related to the absorption $\alpha(\omega) = -\mathrm{Im}\langle\langle G(\omega,R)\rangle\rangle/\pi$, where $\langle\langle\cdots\rangle\rangle$ means average disorder of the Green's function propagator.[2,16–18] For the ground state energies,

$$\alpha(\omega) \simeq \int P(R)\,\delta(\hbar\omega - E_i^0(R))\,dR, \tag{1}$$

where $E_i^0 = E^0(H_3^+) - E^0(H_3)$ is the ionization energy of the lowest state of the three-donor molecules and $P(R)$ is the triad distribution function at separation R; see Refs. 2 and 9. The imaginary part ϵ_2 of the dieletric function is obtained from

$$n(\omega) = n + \frac{1}{\pi}\int_0^\infty \frac{\alpha(\omega')}{\omega'^2 - \omega^2}\,d\omega' \tag{2}$$

$$\epsilon_2(\omega) \simeq 2\,\mathrm{Re}[n(\omega)]\mathrm{Im}[n(\omega)]. \tag{3}$$

The results for $\epsilon_2(\omega)$, which properly describes the positions of the absorption bands, are shown in Fig. 2. Figure 2 includes both the SCF (Ref. 2) and MCSCF model calculations applied to GaAs doped with Si. Also in Fig. 2, $P\epsilon_2$ stands for the peak position, $\Delta\omega$ is the width of the spectrum, $\Delta\omega/P\epsilon_2$ is the relative width, and $P\epsilon_2/E_i$ is the percentage of ionization energy.

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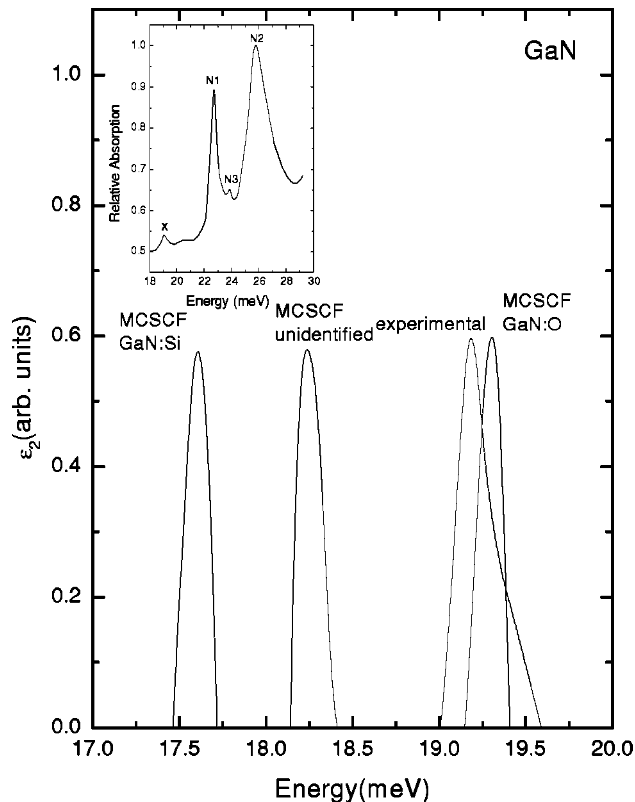

FIG. 3. Imaginary part of the dielectric function for three-donor clusters in n-type GaN. The inset shows the relative absorption given by Moore *et al.* (Ref. 8).

By proper inclusion of electron correlation in the three-donor cluster, we obtained significantly better agreement between the model calculations and the experimental result[1] for the $\epsilon_2(\omega)$. The MCSCF calculation presents a sharper peak around the expected line X, with less dispersion, compared to the corresponding SCF result.[2] This fact can be explained by Fig. 1 and Eq. (1) since the distribution function favors interatomic distances of $2a_0 < R < 6a_0$ with a peak at about $4a_0$. In this interval, the MCSCF ionization energies display smaller dispersion than the corresponding SCF values. According to Eq. (1), the MCSCF absorption peak should therefore be sharper and appear at a higher energy than the corresponding SCF peak, which also is observed in Fig. 2.

There are many discussions about E_i^* and $1s-2p_\pm$ transitions for shallow donor Si, O, and C levels in GaN, i.e., GaN:Si, GaN:O and GaN:C.[4–8] The values obtained from these energies lead to $E_{\rm Si}^* < E_{\rm O}^* < E_{\rm C}^*$. Moreover, Moore *et al.*[8] have found an unidentified N3 donor level $E_{\rm uni}^*$ between $E_{\rm Si}^*$ and $E_{\rm O}^*$, i.e., $E_{\rm Si}^* = 30.18$ meV $< E_{\rm uni}^* = 31.23$ meV $< E_{\rm O}^* = 33.23$ meV. Mireles and Ulloa[6] as well as Wang and Chen[7] have found similar values for $E_{\rm Si}^*$, but $E_{\rm O}^* = 31.4$, $E_{\rm C}^* = 33.7$ meV and $E_{\rm O}^* = 32.4$, $E_{\rm C}^* = 34.0$ meV, respectively. In Fig. 1(b) of Ref. 8, we observed a prominent peak, reproduced here as relative absorption in the inset of Fig. 3, around 19.2 meV, which we will identify as line X. The peak has an intensity of about 25% of the N3 line and about 10% of the other two lines. In the inset of Fig. 3, $E(\rm N1) \equiv E_{\rm Si}^*(1s-2p_\pm)$, $E(\rm N2) \equiv E_{\rm O}^*(1s-2p_\pm)$, and $E(\rm N3) \equiv E_{\rm uni}^*(1s-2p_\pm)$.

From the n-type GaAs, InP, and CdTe systems presented in Ref. 1, as well as from the GaN:Si, GaN:O, and GaN:C systems in Refs. 4–8, we observe that the transitions are roughly related to $E(1s-2p_\pm) \simeq 0.76 E_i^*$ and $E(X) \simeq 0.79 E(1s-2p_\pm)$ which yield

$$E(X) \simeq 0.6 E_i^*. \tag{4}$$

For recent experimental data,[8] we show in Fig. 3, the full curve of the expected line X, and compare it to the corresponding calculated line for different ionization energies that correspond to GaN:Si, GaN:N3, and GaN:O. The calculated MCSCF peak energy $E(X) = 19.3$ meV for the transition derived from the ionization energy of oxygen in GaN (Ref. 8) is in excellent agreement with the experimental finding of around 19.2 meV. Moreover, the transition at 16.7 meV recently found by Moore *et al.*[19] is identified here as $E(X)$ for GaN:Si with $E_{\rm Si}^* = 30.18$ meV.

In conclusion, we have shown that MCSCF calculation in conjunction with a modeled impurity system is a powerful method by which to investigate optical absorption of donor clusters in semiconductors. We have found that (i) it is crucial to take into account the all-electron screening, and by including these correlation effects we can (ii) explain the line X in n-type GaAs at far infrared absorption as Si donor assemblies composed of three-donor clusters, (iii) identify the observed low energy peaks in GaN:O and GaN:Si also as electronic transitions of triad clusters and, moreover, (iv) we predict a transition energy of 18.3 meV of the unidentified donor in n-type GaN. It is worth mentioning here that Franzén[20] has shown that intercluster screening has only a minor effect on the electronic transitions.

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