Optical properties of Mn-doped GaN

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Wide-gap GaN semiconductors with or without Mn impurities are extremely interesting systems for opto- or spintronics applications. We present a theoretical study of the optical properties of $Ga_{1-x}Mn_xN$ in the cubic structure using a supercell of 64 atoms. First-principles calculations based on density functional theory are performed by employing the full-potential linearized augmented plane wave method. To describe the correct insulating ground state of GaN:Mn, the local spin density approximation (LSDA) with the Hubbard-like Coulomb term (LSDA $+U$ method) is applied, in addition to the Jahn-Teller effect. We analyze the density of states, the optical transitions, and the dielectric function (real and imaginary part). The optical absorption coefficient is also studied, and we indicate the appearance of local peaks in the gap related with the magnetic impurities, which we analyze in detail.

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I. INTRODUCTION

Wide energy gap III-V nitride semiconductors GaN, AlN, InN, and their quantum-well structures have received considerable attention due to their device applications in the blue and ultraviolet wavelength range.[1–4] The successful fabrication of the blue light III-IV nitride semiconductor laser was demonstrated by Nakamura *et al.*[1] Additional interest in wide-gap nitride semiconductors arises when they are doped with transition-metal ions, especially Mn, due to their potential use in spintronics devices. For instance, a high ferromagnetic (FM) transition temperature was predicted for GaN:Mn.[5] However, up to now, the experimental reports of FMs in GaN:Mn remain highly controversial (see, for instance, Refs. 6 and 7 for recent publications). We remind the reader that the conventional theory of carrier-mediated ferromagnetism in diluted magnetic semiconductors (DMS)[8] requires the simultaneous presence of localized magnetic moments and delocalized charge carriers. Therefore, precise knowledge of the valence state of doping ions is of crucial importance.

Optical measurements, in connection with a theoretical analysis of the spectroscopic data, provide a very useful tool to analyze impurities in wide-gap semiconductors. Here, we will concentrate on GaN:Mn in zinc-blende structure. GaN in a cubic (zinc-blende) phase can be grown epitaxially on cubic SiC or GaAs. It exhibits a number of very appealing properties for device applications: It has a smaller band gap than the wurtzite phase (by 0.2 eV), it can be easily cleaved, and it has a higher saturated drift velocity.[2–4,9]

The well-established ferromagnetism in the related compound GaAs:Mn is based on the presence of Mn ions in the Mn^{2+} charge state, which provides at the same time local spins $S = 5/2$ and hole charge carriers. In other words, Mn impurities act as shallow acceptor levels in GaAs. In contrast, optical measurements of Mn impurities in GaN have shown Mn to be a deep acceptor level with high ionization energy if the Fermi energy remains close to the valence band.[10–12] That implies that Mn is predominantly in the Mn^{3+} charge state and supplies no holes to the valence band. The Mn^{2+} charge state is only found in n-doped samples.[10,11] On the theoretical site, there are numerous calculations based on density functional theory (DFT) that show a ferromagnetic half-metallic ground state.[13–17] Based on such a ground state, the optical properties of GaN:Mn have also been calculated.[18] However, the metallicity leads to a Drude-like peak that is not observed. Recently, it was shown that only a calculation that simultaneously takes into account the Jahn-Teller effect and the strong Coulomb correlation [by the hybrid density functional theory[19] or the local spin density approximation with the Hubbard-like Coulomb term (LSDA $+U$) method[20]] may reproduce the correct insulating ground state. The Jahn-Teller distortion was confirmed by an x-ray study.[21]

The optical measurements of GaN:Mn indicate a characteristic midgap infrared absorption band at 1.4 eV.[10–12] Up to now, it was mostly interpreted as a local d-d transition.[11] Such transitions are electric-dipole-forbidden and their intensity arises due to the magnetic matrix element, which is, however, much smaller than the former. Therefore, these transitions do not appear in band theory calculations of optical properties, which usually neglect the magnetic matrix element. On the other hand, there are serious doubts as to whether the initial state of the infrared transition at 1.4 eV is of pure Mn^{3+} character. According to a proposal by Dietl[22] and others,[10] it may also consist of Mn^{2+} and a surrounding hole. In the following, we will argue that the controversy of Mn^{3+} versus Mn^{2+} plus a tightly bound hole is artificial since there are enough reasons to expect a considerable mixing between both configurations by configuration interaction (CI). As a consequence, the local states are not of pure d character but of mixed p-d character instead.[19,20] This means that the local optical transitions already become visible by the usual electric dipole matrix element. The present paper is devoted to quantifying this hypothesis by using a DFT-based calculation in the *ab initio* sense.

II. METHOD OF CALCULATION

The calculations are performed using the full potential linearized augmented plane wave (FPLAPW) method. In this method, the unit cell is partitioned into nonoverlapping

muffin-tin spheres around the atomic sites and an interstitial region. Different basis sets are used in these two types of regions. The Kohn-Sham equations based on density functional theory (DFT)[23,24] are solved in a self-consistent scheme.

The lattice constant for the pure semiconductor GaN is optimized using the local spin density approximation (LSDA). We obtain for the zinc-blende structure $a_0 = 4.47$ Å, in good agreement with other calculations and with experiment.[25,26] The orbitals of Ga ($3d^{10}4s^24p^1$) and N ($2s^22p^3$) are treated as valence electrons. For all calculations, the accessible WIEN2K code is used.[27] The optical properties are provided in the OPTIC module.[28] The muffin-tin radii adopted were 1.82 Å (Ga), 1.71 Å (N), and 1.93 Å (Mn). The required precision in total energy was achieved using a large plane-wave (PW) cutoff. In the linear APW method, the relevant convergence parameter is $R_{\mathrm{MT}}K_{\mathrm{max}}$, which was set to 7.

To study GaN:Mn, we use a supercell of 64 atoms. The supercell is constructed of $2 \times 2 \times 2$ elementary cells of the zinc-blende structure. We use a $6 \times 6 \times 6$ k-point mesh. To obtain the correct ground state, we employ the LSDA $+U$ method and allow for the Jahn-Teller effect. The LSDA $+U$ parameters are introduced for Mn with $J = 0.86$ eV and $U = 4$ eV similar to previous work. The value $U = 4$ eV gives representative results for a rather large range of U parameters, reaching from 3 up to 8 eV. For the sake of simplicity, we use the previously published displacement parameters for the Jahn-Teller distortion.[20] The cubic symmetry of the ideal tetrahedra with a distance between Mn and N of 1.938 Å is broken into D_{2d} symmetry with the displacement coordinates $\delta_x = 1.68$ pm and $\delta_z = 1.76$ pm.[20]

The optical properties are deduced from the dielectric function of the semiconductor, meaning from $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, which are, respectively, its real and imaginary parts. The imaginary part of the dielectric function $\epsilon_2(\omega)$ is directly obtained from the electronic structure, using the joint density of states and the optical matrix overlap. The real part of the dielectric function ϵ_1 is then calculated by the Kramers-Kronig relation.

III. RESULTS

The LDA calculation of zinc-blende GaN leads to a gap of 2.0 eV, which does not change if we add Mn. This is considerably smaller than the experimental value of 3.3 eV and is corrected throughout the present calculation by a scissor shift of 1.3 eV.[29] We find a width of the valence band of 7 eV. The density of states (DOS) and the optical properties of that compound were already discussed in several studies; see, for instance, Ref. 30.

Let us now turn to the results for the 64-atom supercell where one Ga is replaced by Mn. That corresponds to a concentration of 1/32, i.e., about 3% of Mn. The corresponding DOS of the LSDA $+U$ calculation with Jahn-Teller (JT) distortion is shown in Fig. 1. It is very similar to previous results that used the full potential local orbital (FPLO) method.[20] The remaining differences are unimportant for the discussion below. They occur because different implementations of LSDA $+U$ are not completely equivalent.

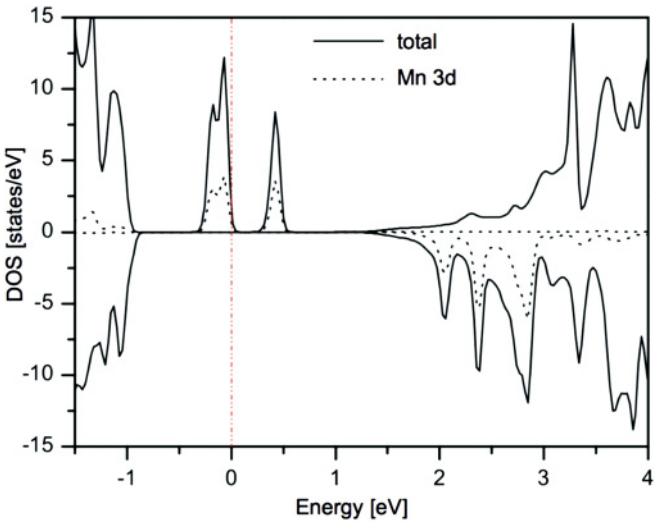

FIG. 1. (Color online) Total density of states of Mn-doped GaN in zinc-blende structure with the Jahn-Teller effect, in LSDA $+U$ ($U = 4$ eV).

The midgap states with spin up (majority spin) arise from the t_2 multiplet, which is split due to the JT effect. The e doublet lies deep in the valence band and is mixed up with the p orbitals. It is visible in Fig. 1 as d weight at about -1.4 eV. The t_2 multiplet is split into a lower doublet just below the Fermi level that is completely filled with electrons and an upper singlet that is empty. The energy difference between the centers of gravity of both bands is about 0.6 eV.

Using the OPTIC module of the WIEN2K package, one obtains directly the imaginary part of the dielectric function ϵ_2 (see Fig. 2 below). The real part is then calculated using the Kramers-Kronig relation. The gap of 3.3 eV is clearly visible in the spectrum of $\epsilon_2(\omega)$ since there are no midgap states with spin down in the DOS (Fig. 1). In contrast, one can see two midgap transitions for spin up. One transition is represented by a separate peak at about 2.5 eV and the other fills in the upper region of the gap (between 3.5 and 4.5 eV). Both transitions are also visible in the optical absorption coefficient (Fig. 3) but are slightly shifted. There, the midgap peak for spin up is located at about 1.9 eV. This corresponds to the transition within the t_2 multiplet, where the peak position is explained by the energy difference of 0.6 eV in the DOS plus the scissor shift of 1.3 eV. The strong p-d mixing is also clearly visible in Fig. 1, which is why the midgap transition appears in our calculation. We interpret that peak as the counterpart of the experimental 1.4 eV transition.

Comparing our calculated absorption curve with the experimental spectra (see Fig. 1 of Ref. 10), we observe a striking similarity. The spin-down curve is not influenced by the midgap transitions and can be compared with the experimental spectra in the absence of Mn^{3+} centers. Mn^{3+} leads to two midgap transitions, both in experiment and in our calculation. The peak at 1.9 eV in Fig. 3 corresponds to peak B in Ref. 10. The same transition is also observed at low temperatures as a zero-phonon line at 1.4 eV.[11] The hybrid density functional study has found an energy separation between the singlet and doublet of 1.46 eV,[19] which is in even better agreement than the present LSDA $+U$ value. In addition, there is a broader

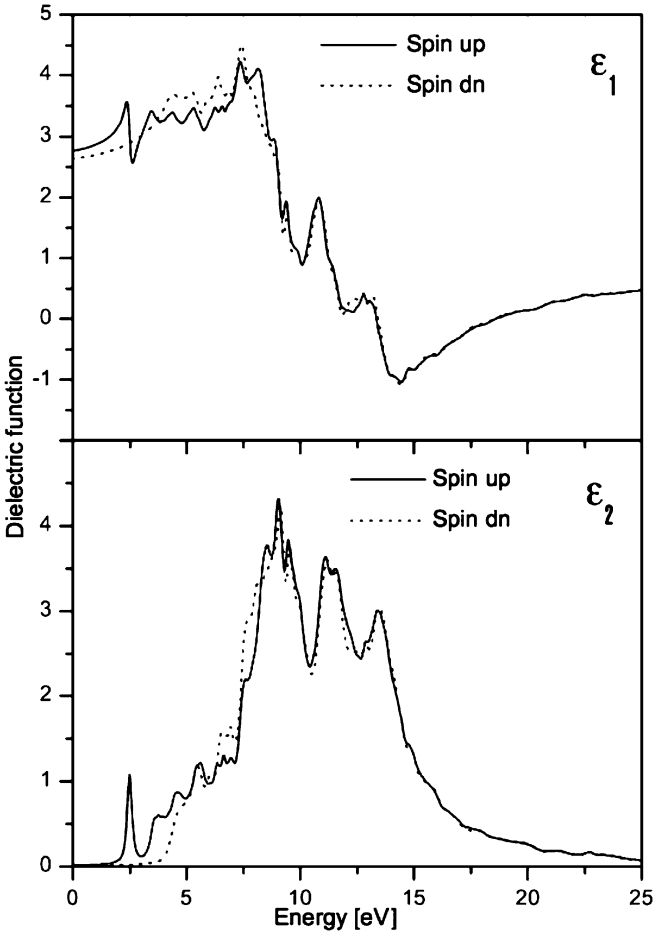

FIG. 2. The real and imaginary part of the dielectric function for spin up and spin down of Mn-doped GaN. Calculated for the zinc-blende structure in LSDA $+U$ ($U = 4$ eV) with the Jahn-Teller effect.

structure A with an energy onset at 1.8 eV in the experiment that fills in the upper part of the gap. That corresponds to the spectral intensity between 3 and 4 eV with spin up in Fig. 3 and is interpreted as transitions from the midgap states to either valence or conduction bands.

IV. DISCUSSION

Even if the present results present an improvement with respect to previous LSDA calculations of optical properties,[18] there remain essential differences between theory and experiment. One of these differences concerns the peak positions, which do not completely agree. Together with the necessity of using the scissor operator, that points to problems in describing exciting states within DFT. It is likely that additional sophisticated methods such as the GW method or hybrid or time-dependent DFT would improve our results further. This was already partially done for the DOS,[19] and it would be interesting to extend that study to optical properties. Another

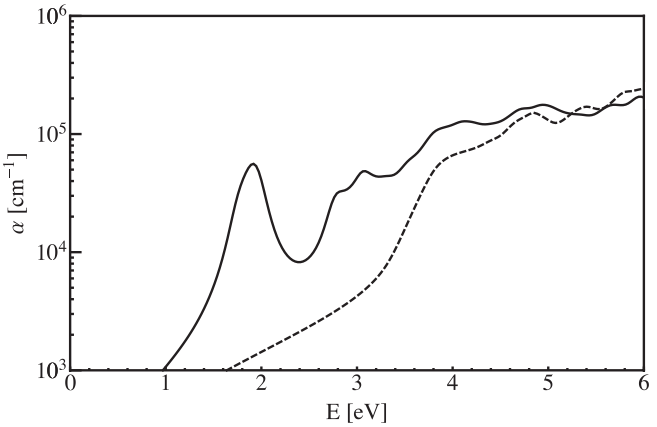

FIG. 3. Optical absorption coefficient for spin up (full line) and spin down (broken line) for Mn-doped GaN in zinc-blende structure with Jahn-Teller effect (LSDA $+U$, $U = 4$ eV).

difference concerns the peak height (at 1.9 eV), which is much larger in Fig. 3 than the corresponding peak B in Ref. 10. But that difference is easily explained since the Mn concentration in our study (3%) is larger than that in the optical measurement of Ref. 10, where it was just 1/4%.

The present method can be generalized in several directions. The treatment of wurtzite GaN:Mn would not encounter any additional difficulty and will most probably lead to similar midgap states, as discussed above. Also, other wide-gap semiconductors with partially filled midgap impurity levels can be treated simultaneously. Finally, we would like to mention the general theoretical problem in describing optical spectra. At present, there are two theories, both quite successful but in clear contrast with each other: band theory and crystal-field theory. We think that the present calculation of optical spectra in GaN:Mn is one step toward closing the gap between these theories.

V. CONCLUSION

Using the FPLAPW method, we calculated the dielectric function and the optical absorption coefficient of GaN:Mn, bringing the theoretical spectra in much better agreement with experiment than previous work. We avoided the artificial Drude-like peak and reproduced the experimental Mn-derived midgap transitions by starting from the correct insulating ground state, which is obtained by treating strong electron correlations (LSDA $+U$ method) and the Jahn-Teller effect on an equal footing. As in experiment, we find two kinds of midgap transitions corresponding to an internal excitation of the Mn center or an excitation to the valence or conduction band. In contrast to previous suggestions, the internal excitation is not of pure d-d character but shows considerable p-d mixing. Our results confirm the conclusion drawn from previous optical measurements[10] that the carrier-induced mechanism of FM in GaN:Mn seems to be unlikely.

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