Polarized photoluminescence study of free and bound excitons in free-standing GaN

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A study of the polarization properties of the exciton emission in GaN is presented. Photoluminescence measurements are performed for light propagation perpendicular to the *c* axis of a free standing layer grown by hydride vapor phase epitaxy. Emission from different polariton branches of the Γ_5 and Γ_1 free exciton states are identified for the $\mathbf{E} \perp \mathbf{c}$ and $\mathbf{E} \| \mathbf{c}$ polarizations, respectively. The mixed-mode transverse-longitudinal state of the A exciton is also observed in the $\mathbf{E} \| \mathbf{c}$ polarized spectra. Donor-bond excitons involving a hole from the A and B valence bands are clearly distinguished and are found to follow the optical selection rules of the free excitons. The temperature dependence of the emission intensities is also investigated and the exciton thermalization processes for both polarizations are discussed.

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The emission properties of GaN have been intensively studied during the last decade. The near-bandgap low-temperature photoluminescence spectrum of an undoped material consists of a number of peaks arising from the recombination of free and bound excitons.[1] Since the energy position, relative intensities, and linewidths of the emission peaks are strongly influenced by the residual strain, crystalline defects, and uncontrolled impurity incorporation, the interpretation of the spectra in heteroepitaxial GaN layers is rather difficult and often leads to confusing conclusions. Recently, with the availability of high quality free standing and homoepitaxial GaN layers, accurate studies and the unambiguous identifications of the emission peaks become possible.[2–5] All these experiments have been performed with a light wave vector **k** parallel to the *c* axis of the crystal and then the excitons with a dipole momentum perpendicular to the *c* axis have been probed. In wurtzite GaN, however, the complex valence band structure and spin-exchange interaction results in five optically active free exciton states, which obey different selection rules.[6] To distinguish between them polarized measurements have to be performed, which is possible if the light wave vector is perpendicular to the *c* axis. So far, there are only a few papers reporting on the GaN emission properties in $\mathbf{k} \perp \mathbf{c}$ geometry.[7–11] The dissimilarity between the $\mathbf{E} \perp \mathbf{c}$ and $\mathbf{E} \| \mathbf{c}$ polarized spectra has been observed in heteroepitaxial[7,9,10] and free standing layers,[8,9,11] but the assignment of the emission peaks, especially for $\mathbf{E} \| \mathbf{c}$, was rather controversial.

In this work, we present results from a temperature-dependent polarized photoluminescence study of a free standing GaN layer. The well-resolved emission peaks in both polarizations allow us to reveal exciton states with different symmetry and to clearly distinguish between the extrinsic and intrinsic emissions.

The sample studied is a crack-free 40-μm-thick GaN layer grown by hydride vapor phase epitaxy (HVPE) on sapphire with a metalorganic chemical vapor deposition (MOCVD) GaN buffer and then separated from the substrate by a laser lift-off technique. The Hall effect measurements revealed electron concentration of 1×10^{17} cm^{-3} at room temperature. The PL spectra were taken in the temperature range 10–150 K with continuous wave optical excitation from a Verdi/MBD-266 laser system ($\lambda = 266$ nm). The laser beam was focused by a microscopic objective on the cleaved edge of the sample (ensuring $\mathbf{k} \perp \mathbf{c}$ geometry) into a spot of ≈ 3 μm diameter. The excitation intensity was in the range 1–10 W/cm^2. The emission was dispersed by a single monochromator and detected by a UV-enhanced charge coupled detector (CCD). The spectral resolution was better than 0.2 meV.

When the light wave vector **k** is perpendicular to the *c* axis of the crystal, the 12-fold degenerated ground exciton state in wurtzite GaN is completely split by the crystal field, spin-orbit interaction, and spin-exchange interaction. Among the 12 exciton states only five are optically active: the three states with Γ_5 symmetry (allowed for the $\mathbf{E} \perp \mathbf{c}$ polarization) and the two states with Γ_1 symmetry (allowed for the $\mathbf{E} \| \mathbf{c}$ polarization). Due to the strong coupling with the photons all dipole-allowed excitons form mixed exciton-polariton states, and the exciton recombination process becomes a propagation of polariton waves to the crystal surface and transmission outside as photons, rather than the transition from the exciton state to the photon state and subsequent photon propagation. Then, the emission linewidth does not reflect the inherent lifetime broadening of the free excitons. The emission peaks are usually quite broad and their line shape (not exactly symmetric) is determined by the spectral dependence of the density of states, group velocity, and transmission coefficient of the different polariton branches. In contrast, when the excitons are bound to a donor or an acceptor the wave function of the complex is strongly localized and sharp emission lines are observed. Because the oscillator strength of a bound exciton is proportional of the oscillator strength of the free exciton from which it is derived, the same selection rules are expected to hold for bound and free excitons.

Figure 1 shows the PL spectra taken for $\mathbf{E} \perp \mathbf{c}$ and $\mathbf{E} \| \mathbf{c}$ polarization in the temperature range 10–60 K. In the case of $\mathbf{E} \perp \mathbf{c}$, the low-temperature spectrum reveals three relative sharp bound-exciton lines at 3.4666, 3.4716, and 3.4753 eV and two broad emission bands peaked at 3.4786 and 3.4834 eV originating from the A and *B* exciton polaritons [Fig. 1(a)]. Low excitation intensity measurements (not shown here) indicate that the dominant emission ($D^{\circ}X_A$) is

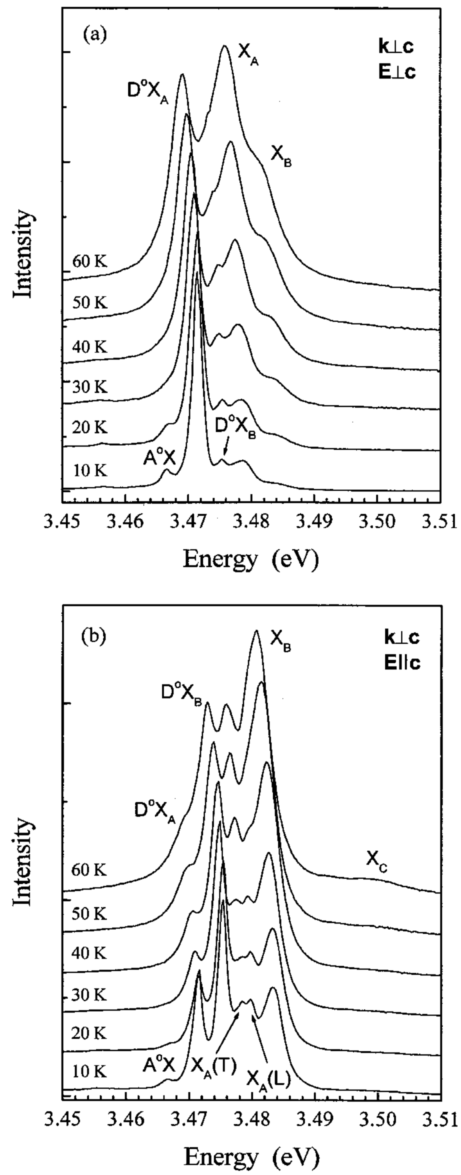

FIG. 1. Photoluminescence spectra of free standing GaN layer for the $\mathbf{E}\perp\mathbf{c}$ (a) and $\mathbf{E}\|\mathbf{c}$ (b) polarizations at different temperatures. The spectra are normalized to the $D°X_A$ (a) and $D°X_B$ (b) peaks and shifted for clarity.

in fact composed of two peaks separated from each other by 0.9 meV and having a full width at half maximum (FWHM) of 0.8 and 1.0 meV, respectively. The peaks are associated with the recombination of the A exciton bound to two shallow donors. Most probably these are the neutral oxygen donor on the N site and the neutral silicon donor on the Ga site, which are commonly identified in HVPE grown GaN layers.[5] The low-energy peak at 3.4666 eV (FWHM=1 meV) is the emission of the A exciton bound to a neutral acceptor ($A°X_A$).[12] Although in some reports this emission is tentatively related to the magnesium acceptor on the Ga site a definite identification of the chemical origin of the acceptor involved in the $A°X_A$ is still missing. The peak at 3.4753 eV (FWHM=1.3 meV) is attributed to the emission of a donor-bound exciton complex of the B exciton ($D°X_B$).[13] The extrinsic nature of this peak is verified by its faster quenching with temperature compared to the exciton-polariton related emission. The relatively high intensity and the large separation from the $D°X_A$ peak (3.8 meV) rules out the possibility that the 3.4753 eV emission could be a rotation excited state of $D°X_A$. Moreover, the $D°X_B$ peak is more strongly pronounced in the $\mathbf{E}\|\mathbf{c}$ polarization (see below) which is consistent with the optical selection rules for the B exciton. It is plausible that the same neutral donors responsible for the $D°X_A$ peak should be involved in the $D°X_B$ emission but we are not able to resolve a doublet structure even at very low excitation intensity.

The exciton-polariton emissions X_A and X_B is believed to arise from the knee regions of the lower polariton branches of the A and B excitons, where the highest radiative efficiency is expected due to the maximum in the polariton population. However, a careful deconvolution of the low-temperature spectrum yields FWHM≈2.5 meV for the X_A emission, which is larger than the expected longitudinal-transversal splitting of the A exciton in strain-free GaN.[6] Then, the contribution from the upper polariton branch cannot be ruled out. Such a large broadening also suggests that no thermal equilibrium between the exciton-polaritons is established at low temperatures, which can be understood having in mind that the density of states of the lower polariton branch has no well-defined low-energy limit.[14] The X_B emission is even broader (FWHM≈3.5 meV) and exhibits a pronounced high-energy tail. This result is attributed to the presence of an additional polariton branch between the original lower and upper branches of the B exciton, which arises due to the k-linear energy term mixing between the Γ_2 state and transverse Γ_5 state (Γ_{5T}) for the $\mathbf{k}\perp\mathbf{c}$ geometry in wurtzite crystals.[15] The calculated dispersion curves of the polaritons associated with the A and B excitons for $\mathbf{k}\perp\mathbf{c}$ and $\mathbf{E}\perp\mathbf{c}$ are shown in Fig. 2(a). (For calculation details see Ref. 16.) We also note that due to the small energy difference between the A and B excitons the upper polariton branch of the A exciton merges with the lower polariton branch of the B exciton forming a combined branch. As a result a spectral region of relatively high polariton population exists between the A and B excitons and the two emission bands are slightly overlapped.

In the case of $\mathbf{E}\|\mathbf{c}$ polarization, quite different PL spectra are obtained [Fig. 1(b)]. The low-temperature spectrum is dominated by the $D°X_B$ enmission at 3.4753 eV (FWHM =1.6 meV). The peak appears at the same energy as in the $\mathbf{E}\perp\mathbf{c}$ polarization, which is not surprising having in mind that the Γ_1 and Γ_5 states of the B exciton are almost degenerated at zero strain.[6] Although the A exciton is dipole forbidden for $\mathbf{E}\|\mathbf{c}$, the emission peaks of $A°X_A$ and $D°X_A$ complexes are still visible at low temperatures implying some relaxation of the selection rules, most probably due to a small misalignment from the $\mathbf{k}\perp\mathbf{c}$ geometry. The latter can also explain the observed variation in the intensity ration between $D°X_B$ and $D°X_A$ peaks when the excitation spot is shifted across the sample. Comparing with the $\mathbf{E}\perp\mathbf{c}$ polarization the exciton-polariton emission is much better pronounced. The main peak X_B occurs from the lower polariton branch of the B exciton (with Γ_1 symmetry), which is the

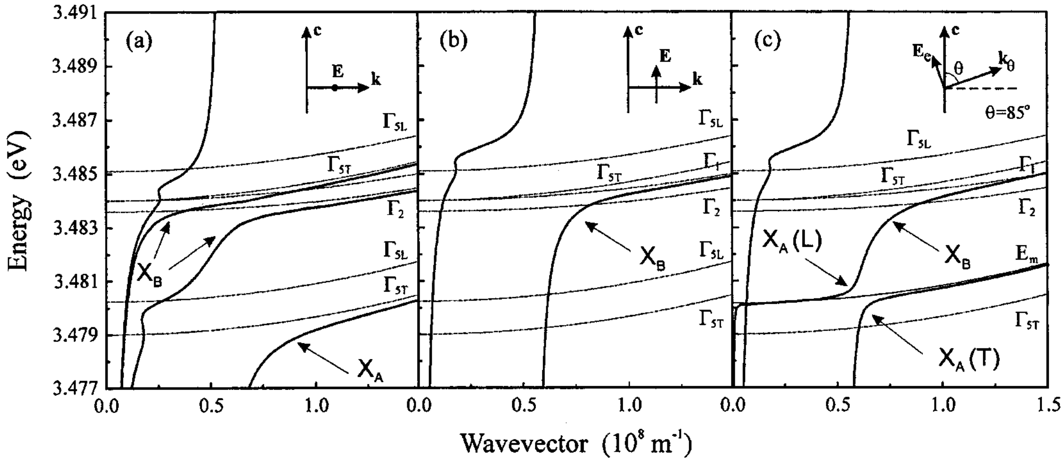

FIG. 2. Dispersion of polaritons arising from the A and B excitons in wurtzite GaN for $\mathbf{E}\perp\mathbf{c}$, $\mathbf{k}\perp\mathbf{c}$ (a), $\mathbf{E}\|\mathbf{c}$, $\mathbf{k}\perp\mathbf{c}$ (b), and $\mathbf{E}\|\mathbf{c}$, $\angle(\mathbf{k},\mathbf{c})=85°$ (c). The dashed lines show the uncoupled exciton states. The arrows indicate the regions where the polariton emission is expected to occur.

lowest optically active branch for the $\mathbf{E}\|\mathbf{c}$ polarization [Fig. 2(b)]. At temperatures above 80 K a weak emission from the upper polariton branch is also resolved.[16] Such a doublet structure of the X_B persists up to 110 K and then the higher-energy peak is taken over by the broad emission X_C originating from the lower polariton branch of the C exciton. The FWHM of the X_B peak at low temperatures (2.5 meV) is smaller than in the case of the $\mathbf{E}\perp\mathbf{c}$ polarization implying no contribution from the k-linear term induced polariton branch. It is worth noting that the k-linear coupling between the Γ_1 state and longitudinal Γ_5 state (Γ_{5L}), which is relevant for the $\mathbf{E}\|\mathbf{c}$ polarization, is expected to be week due to the relatively large energy separation between the coupled states.

Surprisingly, two peaks, labeled $X_A(T)$ and $X_A(L)$, are observed in the energy region of the optically forbidden A exciton [Fig. 1(b)]. These peaks could be interpreted as emissions from the Γ_6 and Γ_{5L} states of the A exciton, which become slightly allowed due to the mixing with the Γ_1 state of the B exciton.[17] However, the temperature dependence of the peak positions, namely, the redshift of $X_A(T)$ and the blueshift of $X_A(L)$, is typical for emissions arising from the lower and upper polariton branches on an exciton polariton. Usually, due to the small density of states of the upper polariton branch there is a fast filling of the polariton states with temperature and the emission occurs at an energy higher than that expected from the thermal redshift. The existence of the A exciton polariton in the $\mathbf{E}\|\mathbf{c}$ polarization can be explained by a slight deviation from $\mathbf{k}\perp\mathbf{c}$ geometry. In such a case, the twofold degenerated Γ_5 state of the A exciton evolves in a purely transverse state (dipole forbidden for $\mathbf{E}\|\mathbf{c}$) and a mixed longitudinal-transverse state E_m. The mixed state can couple with the extraordinary photon polarized in the ($\mathbf{k}$-c axis) plane and as a result two polariton branches are formed.[18] This is illustrated in Fig. 2(c), where the polariton dispersion in the region of the A and B excitons for a 5° misalignment from the $\mathbf{k}\perp\mathbf{c}$ geometry is shown. Hence, the $X_A(T)$ and $X_A(L)$ peaks are attributed to the emissions from the lower and upper branches of the mixed A exciton polariton.

With an excitation above bandgap photogenerated electron-hole pairs relax to the lowest excitonlike polariton branches. From there the excitons are captured by donors or acceptors to form bound complexes or are scattered via acoustic phonon emission toward the knee region of the

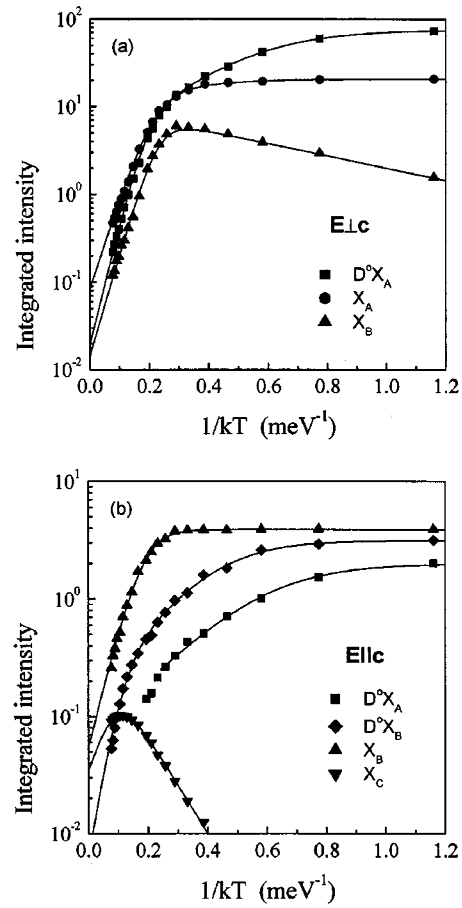

FIG. 3. Temperature dependence of the integrated PL intensity of the donor-bound excitons and exciton-polaritons for the $\mathbf{E}\perp\mathbf{c}$ (a) and $\mathbf{E}\|\mathbf{c}$ (b) polarizations.

lower polariton branches where they recombine radiatively. With increasing temperature the excitons are released from the complexes, increasing the density of the excitonlike polaritons. The density of the photonlike polaritons in the knee region is also increased due to the enhanced acoustic-phonon scattering, and as a result the emission of the exciton-polaritons starts to dominate over the bound exciton emission. To get insight into the thermal redistribution of the excitons we studied the temperature dependence of the integrated intensity of the all emission peaks (Fig. 3). The experimental data are analyzed by the well-known relation for the thermal quenching of the PL intensity $I = C/[1 + \Sigma a_i \exp(E_i/kT)]$, where several nonradiative processes with thermal activation energies E_i can be included.[19,20] The quenching of the donor-bound exciton emissions $D°X_A$ for $\mathbf{E} \perp \mathbf{c}$ and $D°X_B$ for $\mathbf{E} \| \mathbf{c}$ is well described by two nonradiative processes. In the low-temperature range $(T < 35\text{ K})$, a process of the detrapping of the excitons from the complexes occurs with thermal activation energies of 5.8 and 7.2 meV for $D°X_A$ and $D°X_B$, respectively. These values are in a good agreement with the measured optical depths in the low-temperature spectra (Fig. 1). The difference suggests a slightly higher binding energy of the $D°X_B$ exciton probably due to the larger polaron mass of the B valence band.[21] The second nonradiative process with activation energy of about 30 meV for both emissions becomes important at higher temperature and can be attributed to the ionization of the donors or to a simultaneous exciton delocalization and exciton dissociation.[20] The $D°X_A$ emission for $\mathbf{E} \| \mathbf{c}$ cannot be followed in the whole temperature range, but below 60 K its quenching behavior (activation energy of 6 meV) is almost identical to that for $\mathbf{E} \perp \mathbf{c}$ polarization.

The thermal quenching of the A exciton polariton for $\mathbf{E} \perp \mathbf{c}$ polarization is also satisfactorily fitted with two nonradiative processes with activation energies of 6.5 and 24 meV, respectively. The first process is attributed to the enhanced scattering out of the polaritons from the lower branch of the *A* exciton to the polariton branches of the *B* exciton, while the second process reflects the exciton dissociation. The increase of the population in the *B* polariton branches is also evidenced by the enhancement of X_B intensity in the temperature range 10−40 K [Fig. 3(a)]. At higher temperatures the intensity of X_B quenches with the same thermal activation energy as X_A, which is not surprising because the exciton binding energy of the *A* and *B* excitons is almost the same (≈26 meV). In the case of $\mathbf{E} \| \mathbf{c}$ polarization, the temperature dependence of the X_B emission behaves differently [Fig. 3(b)]. The best fit of the experimental data yields single activation energy of 25 meV, which implies that the quenching is mainly due to the exciton dissociation. The increase of the intensity of the X_C emission observed up to $T = 100$ K is then associated with thermalization of the excitons on the excitonlike part of the polariton branches rather than to a scattering out of the *B* polaritons to the lower polariton branch of the *C* exciton.

In summary, we have reported a study of the polarization properties of the near bandgap emission in a high quality free standing GaN layer. We have clearly demonstrated that the emission for the $\mathbf{E} \| \mathbf{c}$ polarization is dominated by the donor-bound excitons and exciton polaritons arising from the Γ_1 state of the *B* exciton. By examination of the thermal quenching of the emissions peaks, a difference in the thermalization processes of the exciton-polaritons polarized perpendicular and parallel to the *c* axis has also been revealed.

[1] B. Monemar, in *Gallium Nitride I*, edited by J. I. Pakove and T. D. Moustakas (Academic Press, San Diego, 1998), p. 305.

[2] K. Kornitzer, T. Ebner, K. Thonke, R. Sauer, C. Kirchner, V. Schwegler, M. Kamp, M. Leszczynski, I. Grzegory, and S. Porovski, Phys. Rev. B **60**, 1471 (1999).

[3] G. Martinez-Criado, C. R. Miskys, A. Cros, O. Ambacher, A. Cantanero, and M. Stutzmann, J. Appl. Phys. **90**, 5627 (2001).

[4] M. Reshchikov, D. Huang, F. Yun, L. He, H. Morkoç, D. C. Reynolds, S. S. Park, and K. Y. Lee, Appl. Phys. Lett. **79**, 3779 (2001).

[5] J. A. Freitas, Jr, W. J. Moore, B. V. Shanabrook, G. C. B. Braga, S. K. Lee, S. S. Park, and J. Y. Han, Phys. Rev. B **66**, 233311 (2002).

[6] B. Gil, in *Gallium Nitride II*, edited by J. I. Pankove and T. D. Moustakas (Academic Press, San Diego, 1999), p. 209.

[7] L. Eckey, A. Hoffmann, P. Thurian, I. Broser, B. K. Meyer, and K. Hiramatsu, in *Nitride Semiconductors*, edited by F. A. Ponce *et al.*, MRS Symp. Proc. No. 482 (Materials Research Society, Warrendale, 1998), p. 555.

[8] D. C. Reynolds, D. C. Look, B. Jogai, A. W. Saxler, S. S. Park, and J. Y. Hahn, Appl. Phys. Lett. **77**, 2879 (2000).

[9] P. P. Paskov, T. Paskova, P. O. Holtz, and B. Monemar, Phys. Rev. B **64**, 115201 (2001).

[10] T. V. Shubina, T. Paskova, A. A. Toropov, S. V. Ivanov, and B. Monemar, Phys. Rev. B **65**, 075212 (2002).

[11] D. C. Reynolds, J. Hoelscher, C. W. Litton, and T. C. Collins, J. Appl. Phys. **92**, 5596 (2002).

[12] B. Monemar, W. M. Chen, P. P. Paskov, T. Paskova, G. Pozina, and J. P. Bergman, Phys. Status Solidi B **228**, 489 (2001).

[13] K. P. Korona, A. Wysmolek, R. Stepniewski, M. Potemski, J. Kuhl, J. M. Baranowski, G. Martinez, I. Grzegory, and S. Porowski, Phys. Status Solidi B **235**, 31 (2003).

[14] U. Heim and P. Wiesner, Phys. Rev. Lett. **30**, 1205 (1973).

[15] G. D. Mahan and J. J. Hopfield, Phys. Rev. **135**, A428 (1964).

[16] P. P. Paskov, T. Paskova, P. O. Holtz, and B. Monemar, Phys. Status Solidi A **201**, 681 (2004).

[17] K. Cho, Phys. Rev. B **14**, 4463 (1976).

[18] C. Benoit a la Guillaume, A. Bonnot, and J. M. Debever, Phys. Rev. Lett. **24**, 1235 (1970).

[19] D. Bimberg, M. Sondergeld, and E. Grobe, Phys. Rev. B **4**, 3451 (1971).

[20] M. Leroux, N. Grandjean, B. Beaumont, G. Nataf, J. Massies, and P. Gibart, J. Appl. Phys. **86**, 3721 (1999).

[21] A. V. Rodina, M. Dietrich, A. Göldner, L. Eckye, A. Hoffmann, Al. L. Efros, M. Rosen, and B. K. Meyer, Phys. Rev. B **64**, 115204 (2001).