Density-of-states investigation of C_8K and occurrence of the interlayer band

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The band structure of C_8K is investigated both experimentally and theoretically. For this purpose we have used low-energy electron-energy-loss spectroscopy (LEELS) on C_8K and also calculated the density of states using the band structure of Ohno, Nakao, and Kamimura (ONK) and the charge density of the occupied conduction band at the center of the Brillouin zone, Γ. It is shown that the ONK band can explain the LEELS spectra satisfactorily. It is proved that the charged density has the features of the interlayer state and thus is very different from the K($4s$) charge density. Thus the ONK band structure is consistent with the x-ray photoemission results of Preil and Fischer.

I. INTRODUCTION

Since the first band-structure calculation of C_8K by Inoshita, Nakao, and Kamimura[1] in 1977 followed by the first-principles self-consistent calculation of Ohno, Nakao, and Kamimura[2] (ONK), many experimental and theoretical researches have been reported to test the ONK band structure.[3–14] Most of the experimental results[3–9] have supported the ONK band structure. However, in 1982 DiVincenzo and Rabii[10] reported a band structure of C_8K different from ONK's, although their calculation was non-self-consistent. In their band structure the K($4s$) band minimum is located 1.8 eV above the Fermi level while in ONK's the nearly three-dimensional Fermi surface in the center of the Brillouin zone coexists with the two-dimensional cylindrical Fermi surfaces of graphite character along the edge of the zone. Then, using the results of the high-energy electron transmission (HET) and x-ray photoelectron spectroscopy, Ritsko and Brucker[11] claimed to support the band structure of DiVincenzo and Rabii. Recently Preil and Fischer[12] measured x-ray photoemission spectra (XPS) of the valence band of C_8K to investigate the K($4s$) character at the Fermi level and found that the s character at the Fermi level is substantially low. From this they argue that the Fermi surface of C_8K is of graphite character. Very recently Takahashi, Gunasekara, and Sagawa performed angle-resolved ultraviolet photoemission spectroscopy (UPS) measurements on a better cleaved face of C_8K which covered nearly the whole Brillouin zone along the layer plain.[13] Their result is in excellent agreement with the dispersion of the bonding and antibonding π bands of ONK below the Fermi level.

The aim of the present paper is to clarify the character of Fermi surfaces from both experimental and theoretical aspects. For this purpose we have performed the measurements of low-energy electron-energy-loss spectroscopy (LEELS) in C_8K on one hand, and calculated the density of states of the ONK band and the charge density of the occupied conduction band at the center of the Brillouin zone Γ on the other. It is first shown that the LEELS spectra coincide well with the HET spectra by Ritsko and Brucker and that they can be explained by the density of states of the ONK band. It is then shown that the charge density of the conduction band at Γ is distributed along the K layers. Thus we call the conduction band of the central region of the Brillouin zone the "interlayer band." Posternak *et al.* pointed out the existence of the interlayer state above the Fermi level in the three models of two-dimensional systems of C_6-Li-C_6, C_6-C_6, and C_6.[15] In this paper we show that the interlayer band exists below the Fermi level in a three-dimensional C_8K system and that it has a large dispersion even along the c axis. In Sec. II we present the experimental results of LEELS of C_8K. In Sec. III the theoretical results of the density of states of the ONK band is presented and compared with LEELS spectra. In Sec. IV the charge-density distribution of the occupied conduction band at Γ point is given and XPS results by Preil and Fischer are discussed. Section V is devoted to discussions.

II. LOW-ENERGY ELECTRON-ENERGY-LOSS SPECTRA

The LEELS spectra of C_8K have been taken with a personal-computer-controlled spectrometer using pulse-count detection, the details of which are described elsewhere.[16] Since the surface of an alkali-metal intercalated compound, especially that of C_8K, is known to deteriorate easily,[17] the specimen was cooled down to 140 K and cleaved just before each measurement. The pressure during the measurements was 8×10^{-9} Pa.

Figure 1 shows the LEELS spectra of C_8K in the C($1s$) and K($2p$) core electron excitation regions together with that of highly oriented pyrolytic graphite (HOPG). Al-

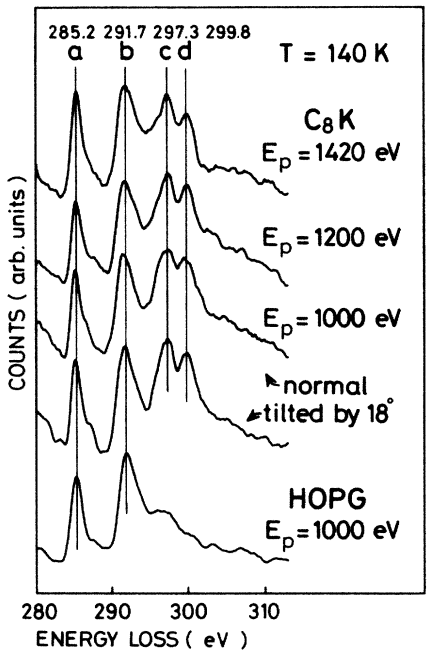

FIG. 1. LEELS spectra of C_8K and highly oriented pyrolytic graphite (HOPG) in the C($1s$) and K($2p$) core-electron excitation region.

though those spectra were taken at 140 K, they are essentially the same as those taken at room temperature, which were reported previously.[14] Since the energy of probing electrons is as high as 1420 eV and the spectra show almost no dependence on the primary electron energy, the observed spectra are considered to arise from bulk origins. Actually, general agreement is obtained between the present spectra and the HET spectrum by Ritsko and Brucker,[11] which reflects only bulk electronic structures.

Since the spectra in the core-electron excitation region is nearly proportional to the imaginary part of the dielectric function ϵ_2,[18] and the width of the core level is very narrow, they will reflect the transition-probability-weighted density of states (DOS) of the final state, that is, conduction and higher band states in the present case. In the LEELS measurement, the inelastic scattering event is preceded or followed by quasielastic scattering from the crystal. Thus wave vectors with various magnitudes and various directions contribute to the LEELS spectrum, and the observed LEELS spectrum in the core-electron excitation region reflects the DOS of the final states averaged over various wave vectors. This tendency is especially emphasized in the LEELS spectrum measured with a cylindrical mirror analyzer, which accepts electrons scattered in a large solid angle. In order to confirm that the observed spectrum is the one averaged rather uniformly over wave vectors, we have changed the primary electron energy from 1000 to 1420 eV and also tilted the sample by 18 degrees from normal to the primary electron beam. Although these changes cause the change in the concerned wave vector as large as 5×10^8 cm^{-1},[19] essentially the same spectra are obtained in Fig. 1, indicating that the observed spectra are not weighted by special k vectors. Thus the spectra seem to reflect the DOS of the conduction band of C_8K in a way similar to the case of graphite and diamond.[18]

As seen in Fig. 1, the peaks a and b are also observed in the C($1s$) core-electron excitation spectrum of graphite, and they are assigned to the electronic transitions from C($1s$) core level at 285 eV below the Fermi level[17] to the graphitelike conduction-band states of C_8K. The final states of the electronic transitions causing the peaks a and b correspond to conduction bands formed from π and σ electrons, respectively, in a way similar to the case of graphite.[18]

The energy separation between the peaks c and d is 2.5 eV, which is very close to that between K($2p_{3/2}$) and K($2p_{1/2}$) core levels observed in the x-ray photoemission spectroscopy.[11] Therefore these peaks are considered to arise from electronic transitions from K($2p$) core levels to the state having the maximum DOS in the K-like conduction band, which will be discussed in the following section.

III. DENSITY OF STATES AND THE CHARGE DENSITY OF THE CONDUCTION BAND AT Γ IN THE ONK BAND

We have calculated the DOS of C_8K using the result of the self-consistent band-structure calculation by ONK. The density of states is defined by

$$D(E)=\sum_n \sum_{\mathbf{k}} \delta(E-\epsilon_n(\mathbf{k})) ,$$

where $\epsilon_n(\mathbf{k})$ is the nth energy band in the ONK band structure. In the actual calculation DOS has been obtained by calculating the eigenvalues at 153 k points in the irreducible section of the Brillouin zone and employing the linear-interpolation technique.[20] The calculated result of DOS near the Fermi level is shown in Fig. 2. The DOS of the valence band is very similar to that of the pure graphite. The peak C_b at -4.0 eV and the peak C_a

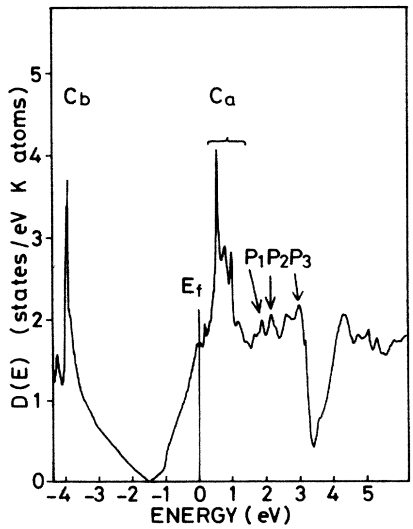

FIG. 2. The density of states of the ONK band near the Fermi level.

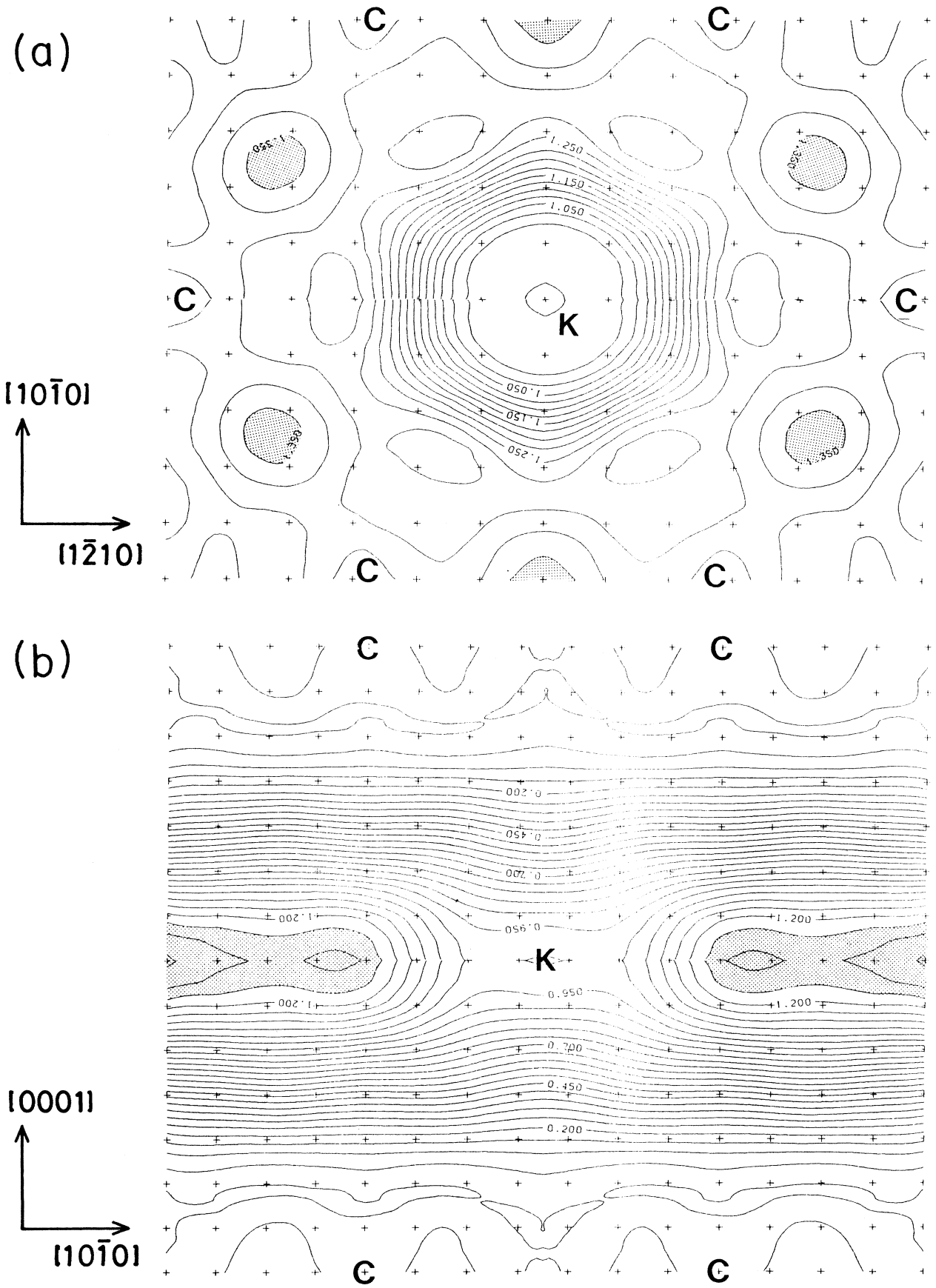

FIG. 3. Charge-density contour plots for the $|1^+\rangle$ state of the ONK band. (a) The top view of the charge density seen along the c axis; (b) the side view seen from the direction perpendicular to the c axis.

at 0.6 eV correspond to the saddle point singularity at the M point of the Brillouin zone of graphite, and the corresponding states have mainly graphite character. The states corresponding to the peaks P_1 through P_3 come mainly from the three-dimensional saddle-point type van Hove singularities of unoccupied conduction bands near the edge of the Brillouin zone.

We have also calculated the charge-density distribution of the occupied conduction band state at Γ point ($k=0$) corresponding to the $|\Gamma_1^+\rangle$ state.[21,22] The top view of this charge density in a potassium layer which is seen from the c axis and its side view perpendicular to the c axis are shown in Figs. 3(a) and 3(b), respectively. It is seen from Fig. 3(a) that the charge density in a K layer has a sixfold symmetry around a K atom but it is the highest in the middle point between two neighboring K atoms and is much lower at a K atom. A more remarkable feature of the charge density is clearly seen from Fig. 3(b), that the charge density is mostly concentrated in a K layer in which it is further concentrated in the regions between K atoms. In this view the charge density of the lowest K-like conduction band state is far from the spherical symmetry and thus very different from that obtained by the potassium $4s$ wave function.

This charge density distribution in the ONK band is similar to that of the interlayer state in the thin-film systems of C_6-Li-C_6, C_6-C_6, and C_6 which appears above the Fermi level and has been interpreted as three-dimensional interlayer states by Posternak *et al.*[15] We also notice the existence of a three-dimensional interlayer band in graphite in the band calculation of Holtzwartz, Louie, and Rabii.[23] In C_8K such an interlayer state also propagates along the c axis by the transfer interaction and it appears below the Fermi level due to the Madelung potential caused by the charge transfer from potassium layers to carbon layers. In the present paper we call this band the interlayer band. In this respect the occupied interlayer band has graphite character and the present result is consistent with the conclusion of Preil and Fischer.[12]

A question arises about the energy position of the K($4s$) band which has also Γ_1^+ symmetry. Since the interlayer band of Γ_1^+ symmetry lies below the K($4s$) band of the same symmetry due to the Madelung potential, the K($4s$) band is further shifted to the higher energy by the off-diagonal repulsive interaction with the interlayer band. It is seen from the ONK bands that the K($4s$) band should be higher than the interlayer band, more than 7 eV at Γ.

The lowest unoccupied conduction band state $|\Gamma_1^-\rangle$ also has graphite character at Γ because $|\Gamma_1^+\rangle$ and $|\Gamma_1^-\rangle$ states correspond to the bonding and antibonding combinations of interlayer states on two inequivalent K layers in a unit cell, respectively. When the wave vector changes from the center of the Brillouin zone Γ to the Brillouin zone edges, the nature of these two interlayer bands also changes from graphite character to the hybridized character of graphite and K($4s$), because the energy difference between the interlayer bands and the K($4s$) band becomes smaller in the ONK band, when the wave vector varies from Γ to the zone edges. Thus for the states of the unoccupied interlayer band $|1^-\rangle$ corresponding to P_1, P_2, and P_3 in the density of states shown in Fig. 2, the K character appears, and the degree of K character in these states increases gradually from P_1 to P_3. Taking account of this fact, we now discuss the LEELS spectra in Fig. 1 in the following section.

IV. COMPARISON WITH LEELS SPECTRA

Let us compare the LEELS spectra in Fig. 1 with the calculated DOS in Fig. 2. Since the degree of mixing of the K($4s$) band increases gradually with increasing energy from Γ along the energy dispersion of the $|1^+\rangle$ antibonding interlayer band, the K character increases from the peaks P_1 to P_3 in the DOS of Fig. 2. Thus we may assign the peaks c and d to the transitions from K($2p_{3/2}$) and K($2p_{1/2}$) core levels to states corresponding to the P_3 region, respectively. From this assignment the energy position of the peak P_3 can be estimated as follows. The low-energy side of peak a shows the onset of electronic transition from the C($1s$) level to the Fermi level E_F, and the energy difference between the C($1s$) level and E_F is estimated as 284.5 eV from the energy of the middle point of the low-energy side of peak a. If we use the value of 9.2 eV for the energy difference between C($1s$) and K($2p_{3/2}$) which was determined by Ritsko and Brucker,[11] the energy difference between the K($2p_{3/2}$) and E_F is estimated as 293.7 eV. Then it is estimated from the observed energy of 297.3 eV for the peak c that the P_3 state is located 3.6 eV above the Fermi level. Thus the agreement between the calculated energy value of the P_3 state (3.0 eV above E_F) and the experimental one is fairly good.

Since HET spectra are nearly the same as LEELS spectra, we can say that the ONK band can also explain HET spectra. Although Ritsko and Brucker assigned the onset of peak c to the transition to the lower K conduction band at Γ, which corresponds to the $|1^+\rangle$ state in the nomenclature of the ONK band in Ref. 2, the $|1^+\rangle$ state is already occupied by electrons and thus the transition cannot occur. Instead, if we assign the onset of the peak c to the transition P_1 state of the unoccupied $|1^-\rangle$ interlayer band for which K character starts to appear, there is no essential inconsistency between the ONK band and HET spectra.

The detailed quantitative comparison between calculated and experimental spectra should be made by calculating $\epsilon_2(\omega)$ directly. In that case we have to take into account the excitonic effect between a hole left in a K core level and a conduction electron in a final state. This will be discussed in Sec. V.

V. DISCUSSIONS

In the present paper we have shown that the ONK band of C_8K can explain recent experimental data of HET, LEELS, and XPS satisfactorily. Here we should mention the excitonic effect in the energy-loss spectroscopy. As pointed out by Mele and Ritsko,[24] the excitonic effect is important in the transition from the C($1s$) core level to the graphite π band, because an electron and a core hole in the final state are located in the same region. Because of this effect the spectrum corresponding to this transition has a very sharp onset. As regards the transition from the K($2p$) core level to the interlayer bands, on the other

hand, the excitonic effect is small on the following grounds. As seen in Fig. 3, electrons in the interlayer band are located in the middle region between K atoms in K layers. Since a core hole in the K($2p$) state exists near the K-atom region, the excitonic effect in the final state is small because of the large distance between the excited electron and the core hole. This is characteristic of a transition in which the interlayer band is involved. Reflecting this fact observed peaks c and d do not have sharp onsets.

Finally, the following fact should be noted. Very recently Tatar[25] and Tatar and Rabii[26] reported another band-structure calculation of C_8K using the density-functional approximation. Their calculations are self-consistent, using the normconserving pseudopotentials. The Fermi surface of C_8K in their calculations is primarily made of trigonal prisms centered along the edge of the Brillouin zone with a secondary, small, narrow, and elongated pocket at the center of the zone. Thus the shape of the Fermi surface in both calculations of ONK and Tatar *et al.* seems similar at a glance, but the character of the central Fermi surface is very different in the sense that it is of a character of interlayer band extending along the K layer in the ONK band while of carbon character extending along the graphite layer in the Tatar-Rabii calculation.[25] It is very difficult to distinguish differences between these two groups by the energy-loss spectroscopy experiment, because the band structure of both groups are very alike.

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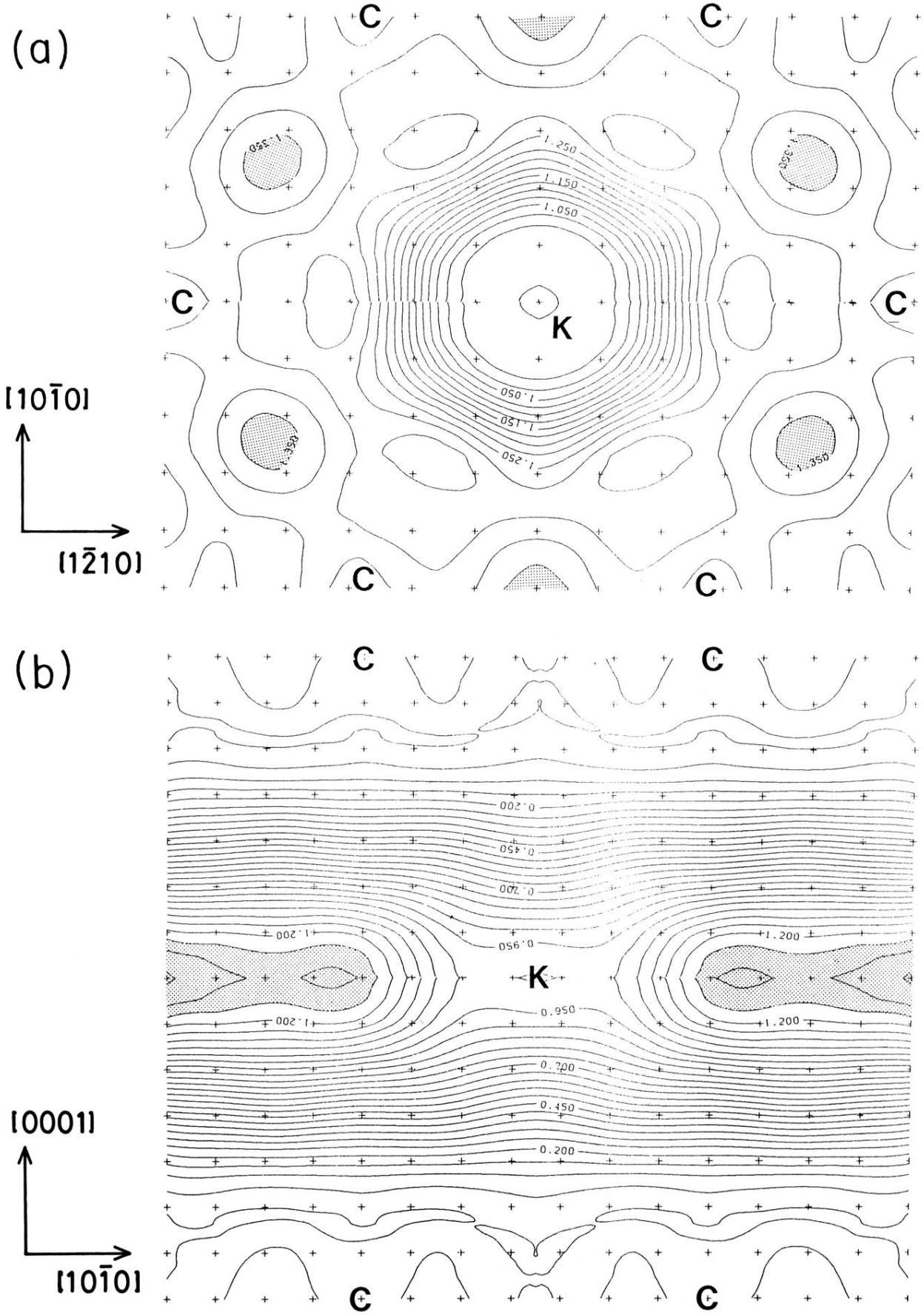

FIG. 3. Charge-density contour plots for the $|1^+\rangle$ state of the ONK band. (a) The top view of the charge density seen along the c axis; (b) the side view seen from the direction perpendicular to the c axis.