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Surface states of LaB_6(001) as revealed by angular-resolved ultraviolet photoelectron spectroscopy

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Surface states of LaB_6(001) have been revealed by angular-resolved ultraviolet photoelectron spectroscopy. An approximate electron angular distribution and energy-band structure of the surface states have been determined. A possible model of the LaB_6(001) surface which is consistent with the experimental results is given. It is pointed out that the origin of the low work function of LaB_6 is probably electric dipole moments produced by surface lanthanum ions.

Lanthanum hexaboride, LaB_6, which is a refractory compound with a low work function has recently become of interest as an electron-beam source of high brightness for various purposes such as microfabrication of superlarge-scale integrated circuits.[1,2]

However, the reason why LaB_6 has such a low work function is still not clear, and in order to solve this problem, we must clarify its surface structure. Furthermore, in using LaB_6 as an electron-beam source, an anticipated problem is the stability of the electron beam which also depends on the surface structure. In addition, the surface structure of LaB_6 is interesting by itself since this compound is unique in that it contains various types of bonds, i.e., covalent (B-B), ionic (B_6-La), and metallic (La-La) bonds.[3] The authors have studied the (001) surface (one of surfaces of low work function[2]) of single-crystal LaB_6 by angular-resolved ultraviolet photoelectron spectroscopy (UPS). This paper is a preliminary report on the results.

UPS and supplemental x-ray photoelectron spectroscopy (XPS) spectra were measured by the V. G. ADES 400-photoelectron spectrometer. Its vacuum chamber could be evacuated down to 4×10^{-11} Torr. A single crystal of LaB_6 was grown by the floating zone method,[4] and a thin sample parallel to the (001) plane was cut from it, and was polished mechanically. In order to clean the sample surface, argon-ion bombardment (1 keV) and electron-beam heating from behind (~1300–1500 °C) were repeated several times in the vacuum chamber, and flash heating (~1300 °C) was done before taking each spectrum. The cleanliness of the surface was confirmed by XPS and low-energy-electron diffraction (LEED); C 1*s* and O 1*s* XPS peaks were not detected at all, and a 1×1 LEED pattern was clearly observed (the LEED experiment was done by a different apparatus). Combined rotations of the sample and the electron analyzer made it possible to measure a spectrum of photoelectrons emitted in any (θ,ϕ) direction, where θ and ϕ are defined in the usual way by taking the Z and X axes as the surface normal ([001]), and the [100] axis of the sample, respectively.

Figure 1 shows UPS spectra taken at various θ's in the (010) plane ($\phi = 0$ °) using He I ($h\nu = 21.2$ eV) as exciting light. Spectra in the $(1\bar{1}0)$ plane ($\phi = 45°$) were also measured (not shown). The incident angle of the exciting light α was 20° from the surface normal (refer to Fig. 2). Most peaks in the spectra are due to bulk energy bands, but the sharp peak appearing at ~2 eV below the Fermi level E_F is attributable to a surface state for the following reasons. First, this peak disappeared by oxygen exposure of ~$7L$ ($L \equiv 10^{-6}$ Torr sec). Second, this peak was observed at fairly high intensity even at large θ such as ~80°. Third, according to energy-band calculations of LaB_6,[5,6] no bulk peak is expected from ~1 to ~3.5 eV below E_F; these energy-band calculations are reliable since the shape of the Fermi surface predicted by the calculations shows a good agreement with experimental one.[5,7] This surface-state peak was also observed when He II, Ne I, or Ne II ($h\nu$ = 40.8, 16.8, or 26.9 eV, respectively,) was used as exciting light.

The θ dependences of the intensity (area) of the surface-state peak, $I(\theta)$, are shown in Figs. 2(a) and 2(b) by filled circles. According to a theory by Gadzuk,[8] $I(\theta)$ is proportional to $\langle\cos^2\gamma\rangle|Y(\theta,\phi)|^2$, where γ is an angle between the vector potential $\vec{A}$ of the exciting light and the direction of the electron analyzer, $\langle\ \rangle$ denotes the average over all directions of $\vec{A}$, and $Y(\theta,\phi)$ is the angular part of an atomic orbital appearing in a tight-binding Bloch function which is used to describe the surface state. If this picture is appropriate, since in our experimental condition $\langle\cos^2\gamma\rangle \propto \sin^2(\alpha+\theta)$ holds, the curves representing $I(\theta)/\sin^2(\alpha+\theta)$ in Figs. 2(a) and 2(b) are proportional to $|Y(\theta,\phi)|^2$ and can be called electron angular distribution (EAD) curves. However, since backscattering

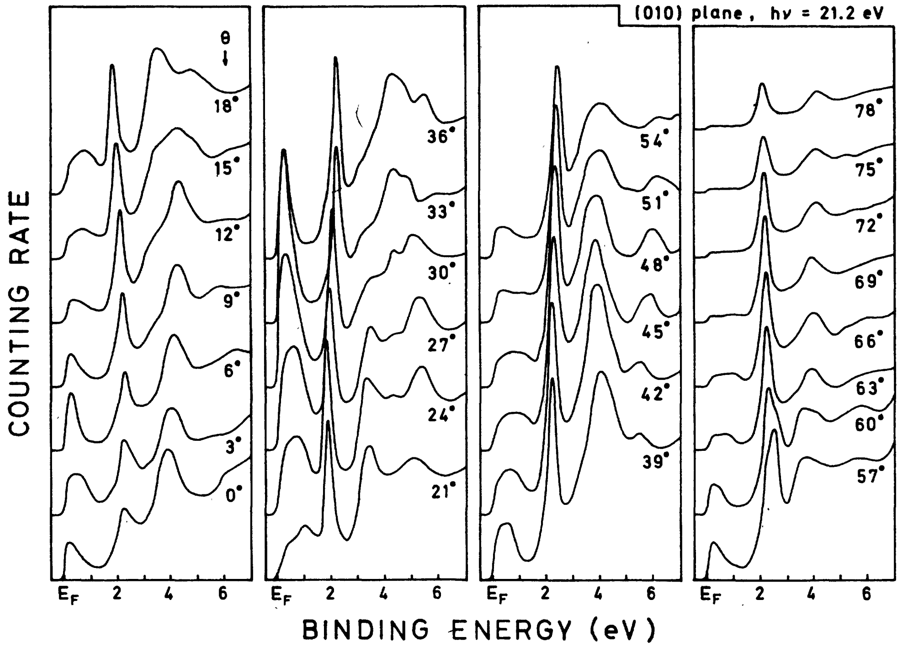

FIG. 1. UPS spectra for the $\mathrm{LaB_6}$(001) surface as a function of θ for $\phi = 0°$ [(010) plane]. The incident angle of the exciting light (He I, $h\nu = 21.2$ eV) α is 20° from the surface normal.

effects of photoelectrons are not negligible as shown by Liebsch,[9] the EAD curves are more or less distorted from their intrinsic shapes, and hence we must be careful in interpreting the curves.

If we assume that the electron momentum parallel to the surface is conserved before and after photoemission, the structure of a two-dimensional energy band which is formed by the surface state can be determined from the θ dependences of the energy position of the surface-state peak (Smith and Traum[10] demonstrated this kind of possibility), and the result is shown in Fig. 3; the insert shows the first Brillouin zone. In the figure, two energy bands appear. This is because the surface-state peak really consists of two peaks. In most spectra, either of the two peaks is predominant, but in the spectra at $\theta = 57$ and 60° in Fig. 1, we can see the two peaks. Even in the latter case, only the energy position of a stronger peak can be determined, and hence, one spectrum and one experimental point in Fig. 3 correspond to each other.

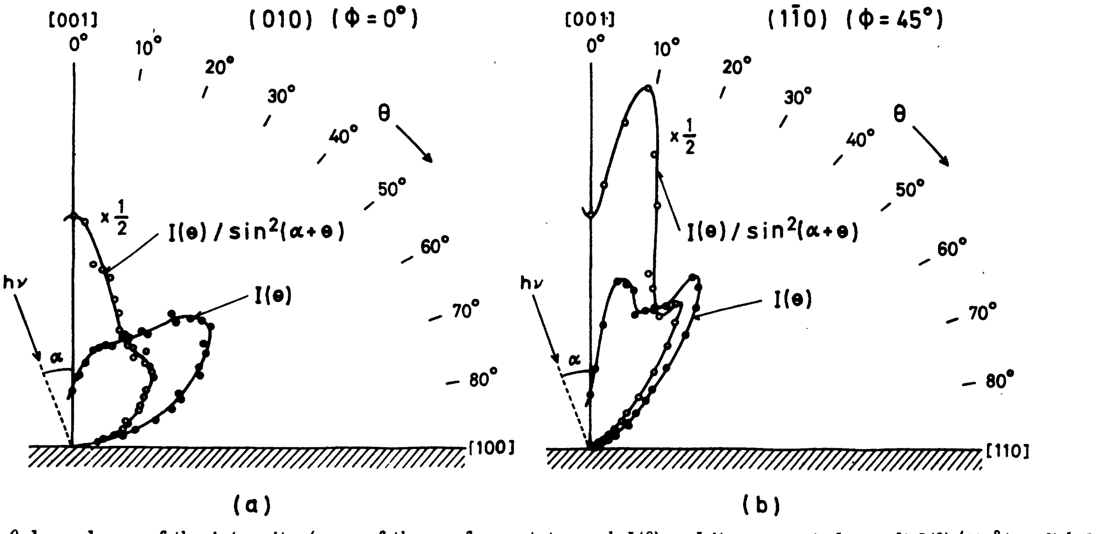

FIG. 2. θ dependence of the intensity (area of the surface-state peak $I(\theta)$ and its corrected result $I(\theta)/\sin^2(\alpha + \theta)$ [electron angular distribution] for (a) $\phi = 0°$ [(010) plane], or (b) $\phi = 45°$ [(1$\bar{1}$0) plane].

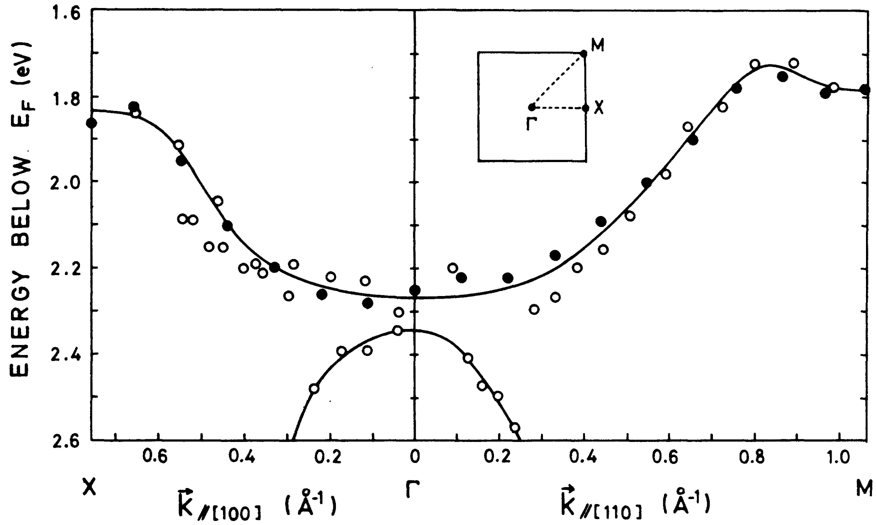

FIG. 3. Structure of two-dimensional energy bands of the $LaB_6(001)$ surface. The experimental points shown by open circles have been reduced from higher Brillouin zones to the first zone.

If we plot the experimental points straightforwardly, some of them go into higher Brillouin zones beyond the first zone. The experimental points shown by open circles have been reduced from the higher zones to the first zone, and they show a good agreement with those in the first zone shown by filled circles. This is a beautiful demonstration of the extended-zone nature of the state. At the same time, the conservation of the electron momentum parallel to the surface is demonstrated.

By noticing that each experimental point in Figs. 2(a) and 2(b) corresponds to that of Fig. 3, it is found that the main lobe at $\theta = 0°$ and the side lobe at $\theta \sim 50°$ of the EAD curve in Fig. 2(a) correspond to the upper and lower energy bands in Fig. 3, respectively. This statement is also substantially true for the EAD curve in Fig. 2(b), although in this case the main lobe inclines at ~8°, and the side lobe suddenly diminishes as θ increases.

A possible model of the LaB_6 (001) surface which is consistent with these experimental results is shown in Fig. 4. As to the bulk electronic structure of LaB_6, it is known that the boron framework takes up electrons from lanthanum atoms so as to complete its B–B covalent bonds.[11] It is therefore reasonable to think that the surface states under consideration associate with electrons of surface boron atoms at such positions as P, P', P'', ... The upper energy band in Fig. 3 and the main lobes of the EAD curves in Figs. 2(a) and 2(b) are supposed to arise from dangling-bond electrons of such surface boron atoms. However, if the upper energy band were formed only by the boron dangling bonds, the band width in the ΓM direction would be smaller than that in the ΓX direction being in conflict with the experimental result of Fig. 3, since the coupling between the boron dangling bonds along P-P'' is expected to be weaker than that along P-P'. This conflict can be removed if we assume the existence of surface lanthanum ions at such a position as R, and consider the coupling P-R-P'' (B-La-B). This coupling means that elec-

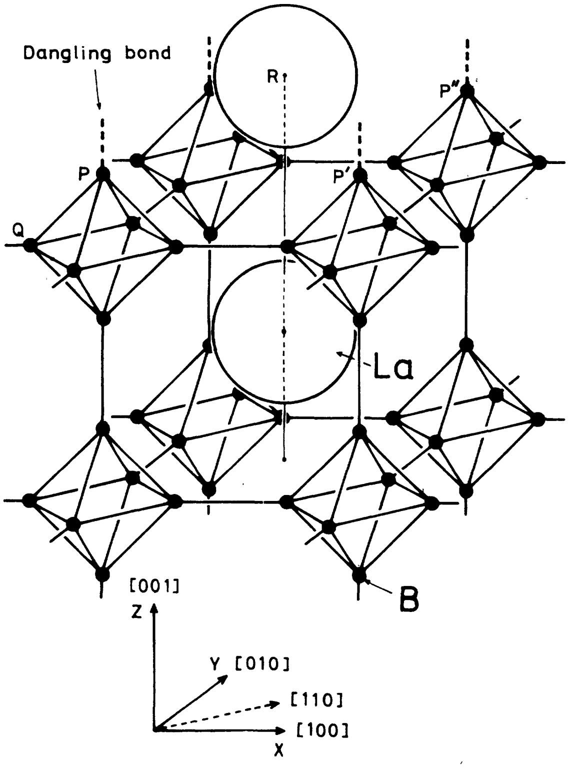

FIG. 4. Possible model of the $LaB_6(001)$ surface which is consistent with the experimental results; the upper side is the surface.

trons of the boron dangling bonds partly enter lanthanum-ion orbitals. This is probably the reason why the EAD curve in the $(1\bar{1}0)$ plane shown in Fig. 2(b) has the inclined main lobe. It is expected that photoelectrons emitted from the surface boron atom atom at P are shielded by the surface lanthanum ion at R in directions near the direction PR. Although this "shadowing effect" has still not been theoretically studied, this may be the reason why the EAD curve in the $(1\bar{1}0)$ plane shown in Fig. 2(b) exhibits the sudden diminution as θ increases. The origin of the other surface state corresponding to the lower energy band in Fig. 3 and the side lobes of the EAD curves in Figs. 2(a) and 2(b) is not clear, but as a possibility, we can think of back bonds such as P-Q. Finally, the origin of the low work function of LaB_6 is probably electric dipole moments produced by the surface lanthanum ions as proposed by Lafferty[12] and by Swanson and Dickinson.[2]

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