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Reinterpretation of a controversial structure in the photoemission spectrum of Ni(001) by spin analysis

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We have performed spin-polarized angle- and energy-resolved photoemission measurements on Ni(001) with polarized He I radiation ($h\nu=21.22$ eV). The energy-distribution curves show a shoulder which has been interpreted heretofore as a $\bar{\Gamma}_5$ *majority-spin* surface state. This surface state was assumed to determine the spin polarization of earlier photoyield measurements near threshold. Our spin-resolved measurements demonstrate, however, that this structure is due to *minority-spin* emission in contradiction to the earlier assignment. Investigations of the light-polarization dependence, as well as of small deviations from normal-emission conditions in conjunction with photoemission calculations, show that the main contributions to the observed structure are due to off-normal emission from the Δ_2 band. It is concluded that contributions from surface structures can only be of minor importance.

I. INTRODUCTION

Angle-resolved photoemission spectroscopy (ARPES) has proved to be a powerful tool in determining the electronic structure of solids and surfaces. However, the identification of different spin states in conventional ARPES must be guided by band structure and photoemission calculations since the spin polarization of the emitted electrons is not determined.[1] This identification of spin states by ARPES is quite developed and reliable in the case of bulk band states, although for small values of the exchange splittings as in Ni a line-shape analysis is difficult and doubtful. On the other hand, the calculations of surface states on metals are still controversial[2–4] and not developed to a state where they can be used with confidence to identify magnetic surface states in photoemission spectra.[1] Three criteria are used for identifying a peak as being due to a surface state:[1] (i) The state must be two-dimensional, i.e., there should be no dispersion in the initial-state energy with $h\nu$ for fixed $\vec{k}_{\parallel}$. (ii) A surface state should be sensitive to the conditions of the surface, e.g., to adsorption. (iii) The state should lie in a gap of the corresponding symmetry in the projection of the bulk band structure onto the surface Brillouin zone (SBZ). A structure which fulfills the first two criteria but not the third one may be a surface resonance. So the most important criterion for a surface *state* is the third one.

In many cases, the identification of a surface state is strongly based on the assignment of the experimentally observed structure to a special spin state since the corresponding band gap exists only for this spin state. At this point the detection of the spin polarization of such a structure becomes crucial for its unambiguous identification. The spin detection is now possible by the recently developed[5,6] technique of spin-polarized angle- and energy-resolved photoemission.

In this work we have applied the method of spin-polarized angle- and energy-resolved photoemission to investigate the controversial nature of a structure observed in normal-emission spectra from Ni(001) just below the Fermi energy. This structure has been ascribed to a majority-spin $\bar{\Gamma}_5$ ($=\Delta_5$) surface state by Erskine[7] using an interpretation based on a non—self-consistent thin-film calculation by Dempsey and Kleinman.[8] It was also suggested to be responsible for the sign reversal in the spin polarization of the first photoyield measurements of Eib and Alvarado.[9] On the other hand, Plummer and Eberhardt[10] could not identify this surface state at $\bar{\Gamma}$, the center of the SBZ. In a self-consistent thin-film calculation Jepsen *et al.*[2] also did not find a corresponding surface state at $\bar{\Gamma}$. These authors ascribe the structure observed by Erskine to a Δ_1 surface *resonance* which appears in their calculation.

According to the controversial points mentioned above there are two aspects which must be proved experimentally to identify the observed structure. Firstly, it must be checked whether the structure is due to majority-spin emission as assumed by Erskine. Secondly, it must be checked whether the structure appears with *s*-polarized or *p*-polarized light. The coupling to *s*-polarized light would emphasize the explanation as a structure of Δ_5 symmetry and contradict the explanation as a Δ_1 surface resonance, since in normal emission only the Δ_5 states contribute to the spectra with *s*-polarized light and the Δ_1 states couple to *p*-polarized light.

II. EXPERIMENTAL

To clarify the above points we have measured the spin-resolved energy-distribution curves (spin-resolved EDC's) in normal emission from Ni(001) with linearly polarized He I radiation ($h\nu=21.22$ eV) from a resonance lamp.

The energy resolution is about 100 meV and the acceptance cone of the spectrometer is $\Delta\theta = \pm 3°$. The sample was a (001)-oriented Ni single crystal having a so-called "picture-frame" shape with its legs oriented in $\langle 110 \rangle$ directions (Fig. 1). A coil was wound around one of its legs for magnetizing the sample. This geometry allows the measurements to be performed without an external magnetic field, i.e., with minimal magnetic stray fields. The Ni crystal was spark cut and aligned to approximately ±1° using standard Laue techniques. The surface normal of the sample was aligned for normal emission within ±0.5° with respect to the electron optical axis of the energy analyzer. The sample was cleaned *in situ* by Ne-ion sputtering and heating cycles with subsequent flashing. The structure of the surface and the cleanliness were checked by low-energy-electron-diffraction and Auger-electron spectroscopy. The base pressure in the system was 2×10^{-10} Torr.

We have measured normal-emission spectra with different degrees of *p* polarization of the light, with different adsorbate coverages of the surface, and also off-normal-emission spectra. For the spectra with *s*-polarized light the photons impinge on the (001) surface with an angle of 30° in the $[1\bar{1}0]$ azimuth with respect to the surface normal and the electric field vector perpendicular to this in the [110] direction [position (a) in Fig. 1]. Spectra with two different degrees of *p* polarization were measured [position (b) in Fig. 1]. In the spectra with the low degree of *p* polarization, unpolarized light impinges at an angle of 60° in the [110] azimuth. In the spectra with the high degree of *p* polarization the angle of incidence is 60° in the [110] azimuth and the light is linearly polarized with the electric field vector in the plane of incidence. In the off-normal-emission spectra the sample is rotated by 5° around the $[1\bar{1}0]$ direction so that unpolarized light impinges under an angle of 55° in the [110] azimuth. Further details of the experimental setup may be found in Refs. 6 and 11.

III. EXPERIMENTAL RESULTS AND INTERPRETATION

Normal emission from the (001) surface must be discussed in terms of the band structure along $\Gamma(\Delta)X$. The corresponding majority-spin band structure is shown in Fig. 2. The initial states include self-energy corrections along the lines proposed by Liebsch.[12] The exact calculation is described in Ref. 13, and starts from the bulk majority-spin muffin-tin potential of Moruzzi *et al.*[14]

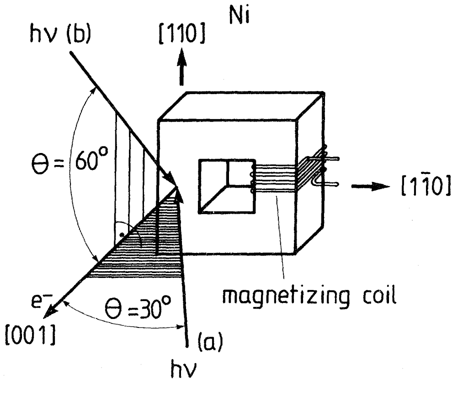

FIG. 1. Schematic drawing of the geometry of the photoemission measurements using a so-called "picture-frame" Ni single crystal. The two different directions (a) and (b) of incident light are shown.

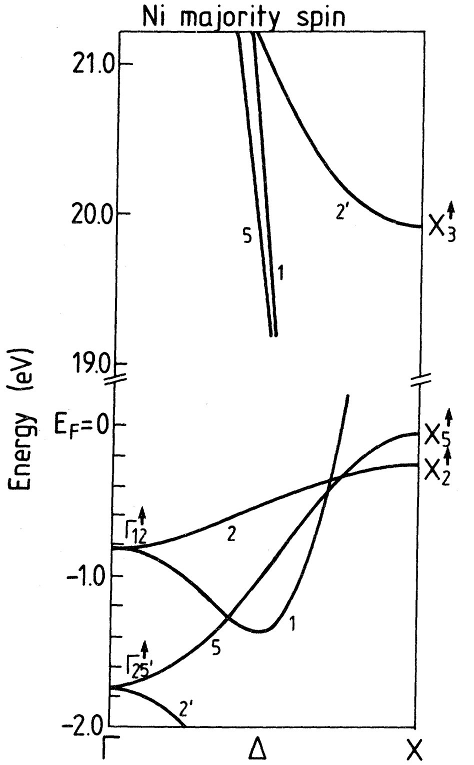

FIG. 2. Majority-spin band structure along $\Gamma(\Delta)X$ including self-energy corrections for the initial states. The displayed final states are those corresponding to an excitation energy of $h\nu = 21.22$ eV.

From the dipole selection rules and the band structure we find that in normal emission there should be only one peak for each spin direction in the spectra with *s*-polarized light corresponding to the direct transition from the Δ_5 initial-state band to the Δ_1 final-state band at about the middle between Γ and X. In contrast to this expectation the spectra [Fig. 3(a)] show two peaks for each spin direction. It is the peak closer to E_F which gives rise to the shoulder observed in the spin-unresolved EDC and this shoulder was interpreted by Erskine as a majority-spin $\bar{\Gamma}_5$ $(=\Delta_5)$ surface state. The fact that the unexplained peak appears for both spin directions is incompatible with the explanation as a surface state since there is no gap in the projection of the minority-spin bulk band structure onto the $\bar{\Gamma}$ point of the SBZ.[10]

For contributions of *p*-polarized light the appearance of an additional peak further below the Fermi energy than the Δ_5 peak is expected, according to the direct transition from the Δ_1 initial-state band to the Δ_1 final-state band. The intensity of this structure in relation to the Δ_5 structure should increase with the degree of *p* polarization. This behavior is clearly revealed in the spectra shown in Figs. 3(b) and 3(c) which belong to two different degrees of *p* polarization. Comparing the intensities of the two

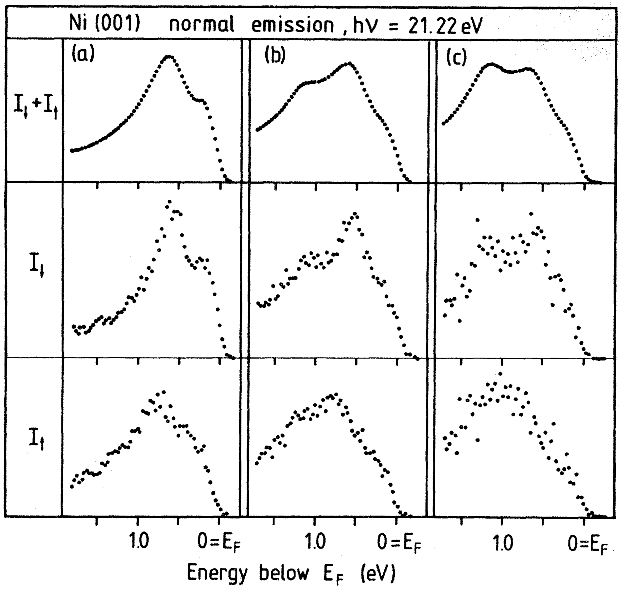

FIG. 3. Angle- and spin-resolved EDC's (in arbitrary units, but identical for spin-up and spin-down spectra) for normal emission from Ni(001) and (a) *s*-polarized light (electric field vector parallel to the [110] direction); (b) unpolarized light impinging under an angle of 60° in the [110] direction relative to the surface normal (small degree of *p* polarization); (c) linearly polarized light impinging under an angle of 60° in the [110] direction relative to the surface normal and with the electric field vector in the plane of incidence (strong degree of *p* polarization).

peaks from the *s*-polarized spectra relative to each other with increasing degree of *p* polarization [Figs. 3(b) and 3(c)] no increase in the relative intensity of the unexplained structure is detected. We therefore conclude that the unexplained structure couples to *s*-polarized light and not to *p*-polarized light. Thus, the observed structure cannot be of Δ_1 symmetry, i.e., it is not a Δ_1 surface resonance as assumed by Jepsen *et al.*[2]

When restricting the discussion to strictly normal emission, i.e., by neglecting the acceptance cone of the spectrometer, the only possible explanation would be an exchange-split Δ_5 surface resonance. In the experiment there is of course a finite acceptance cone ($\Delta\theta = \pm 3°$) and the possibility of off-normal-emission contributions must be checked. Experimentally this was done by measuring spectra under a polar angle of 5° in the [110] direction using unpolarized light impinging at an angle of 55° in the [110] azimuth. The corresponding spectra are shown in Fig. 4 and should be compared to those of Fig. 3(b). They clearly reveal a strong increase in the intensity of the as-yet unexplained peak in comparison to the intensity of the Δ_5 bulk peak. A Δ_5 surface resonance should show an angular dependence similar to that of a Δ_5 bulk state. The observed increase in relative and absolute intensity for a small deviation from normal emission is not expected for any state of Δ_5 symmetry. Such behavior is typical for emission from a state which is forbidden as an initial state under normal-emission conditions. In the bulk band structure there is one such forbidden initial state at energies compatible with the observed spin-split structure. This is the Δ_2 band.

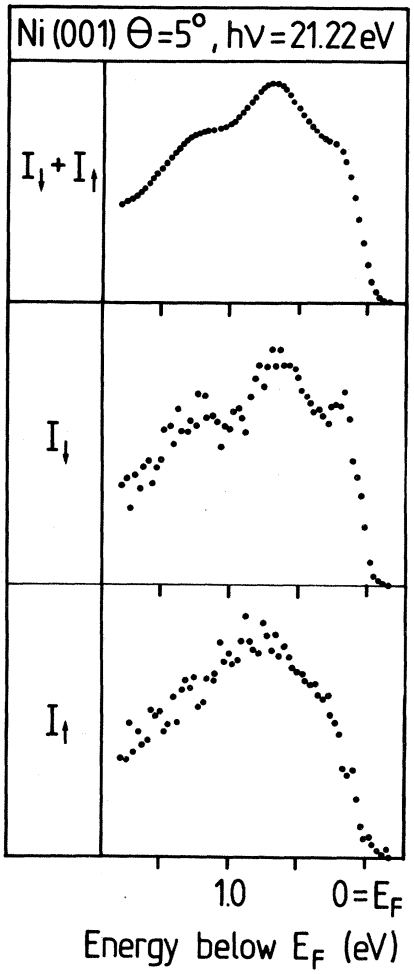

FIG. 4. Angle- and spin-resolved EDC's for off-normal emission from Ni(001). The polar angle is $\theta = 5°$ and the emission is in the [110] direction. The light is unpolarized and impinges under an angle of 55° in the [110] direction relative to the surface normal.

For a theoretical investigation of the emission contributions from this band under off-normal-emission conditions we have used a single-step model of the photoemission process, including self-energy corrections, which was already successfully used in the analysis of spin-polarized angle- and energy-resolved photoemission from Ni(110) (Ref. 13). The sample is treated as a perfect semi-infinite crystal. The calculations start from a bulk muffin-tin potential and include possible surface resonances, while surface states are explicitly excluded from the calculations. Figure 5 shows the calculated minority-spin spectra for *s*-polarized light with the electric field vector parallel to the [110] direction, a polar angle of $\theta = 2°$, and emission summed over the high-symmetry azimuthal directions of [100] and [010] [Fig. 5(a)] and of [110] and $[1\bar{1}0]$ [Fig. 5(b)]. A lifetime broadening for the initial states is not included in the calculations since they are only meant to demonstrate the effects of off-normal emission. A quantitative comparison with the experiment would require an integration over the full acceptance cone of the experiment which was not carried out here. The $\langle 110 \rangle$ directions correspond to the $\bar{\Gamma}(\bar{\Delta})\bar{X}$ directions of the SBZ. The

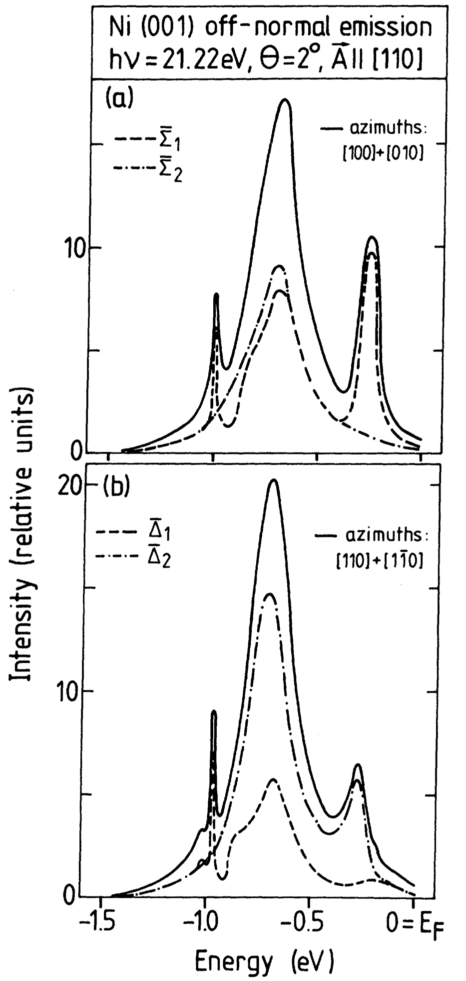

FIG. 5. Calculated minority-spin EDC's for off-normal emission from Ni(001). The light is *s* polarized with the electric field vector parallel to [110]. The polar angle is $\theta=2°$ with respect to the surface normal and the emission is summed (shown by solid line) over the azimuthal directions of (a) [100] and [010] and of (b) [110] and [1$\bar{1}$0]. The contributions from states of $\bar{\Delta}_1$, $\bar{\Sigma}_1$ symmetry (shown by dashed line) and of $\bar{\Delta}_2$, $\bar{\Sigma}_2$ symmetry (shown by the dashed dotted line) are shown separately. No lifetime broadening of the initial states is included.

only symmetry operation for this direction is the reflection in the symmetry plane perpendicular to this direction. Accordingly there are two different symmetries to which the bands belong: the $\bar{\Delta}_1$ bands with even parity with respect to the symmetry operation and the $\bar{\Delta}_2$ bands with odd parity. Similarly, the $\langle 100 \rangle$ directions correspond to the $\bar{\Gamma}(\bar{\Sigma})\bar{M}$ directions of the SBZ. Here we have to distinguish the $\bar{\Sigma}_1$ bands of even parity with respect to the reflection in the symmetry plane perpendicular to these directions and the $\bar{\Sigma}_2$ bands with odd parity. The spectra summed over the chosen azimuthal directions show three peaks instead of the single peak expected for normal emission. The very sharp structure farthest away from E_F is found to be a $\bar{\Delta}_1$ surface resonance ($\bar{\Gamma}\bar{X}$ direction) or a $\bar{\Sigma}_1$ surface resonance ($\bar{\Gamma}\bar{M}$ direction), respectively. Since we have used a simple bulk potential in the calculations this structure cannot be taken too seriously and we do not expect to find a related structure in the experimental spectra [see Fig. 3(a)]. Figure 5 also shows the separate contributions of $\bar{\Delta}_1$, $\bar{\Delta}_2$, $\bar{\Sigma}_1$, and $\bar{\Sigma}_2$ states to the spectra.

From the character tables of the corresponding irreducible representations[15] we find that at the $\bar{\Gamma}$ point (Δ line) the $\bar{\Delta}_1$ states are compatible with the Δ_1 and the $\Delta_{2'}$ bands, the $\bar{\Delta}_2$ states with the Δ_2 and $\Delta_{1'}$ bands, the $\bar{\Sigma}_1$ states with the Δ_1 and Δ_2 bands, and the $\bar{\Sigma}_2$ states with the $\Delta_{1'}$ and $\Delta_{2'}$ bands. The degenerate Δ_5 band splits away from $\bar{\Gamma}$ into two separate bands, each belonging to one of the two different symmetries of the high-symmetry lines. A detailed analysis of the calculated spectra shows that the main peak, which appears in each of the spectra, is related to the bands which become the Δ_5 band at $\bar{\Gamma}$. The peak closer to E_F, originating from $\bar{\Delta}_2$ and $\bar{\Sigma}_1$ states, is related to the Δ_2 band at $\bar{\Gamma}$. The positions of the two peaks are in reasonable agreement with the experimental minority-spin spectrum. The slight shift to higher binding energies agrees with the observations for the analysis of the Ni(110) spectra[13] and is ascribed to an underestimation of the self-energy corrections. The analysis of the azimuthal dependence of the Δ_2 peak intensity (Fig. 6) shows that Fig. 5(b) displays the minimum in the relative intensities between the Δ_2 and Δ_5 peaks. For most of the azimuthal angles the situation is closer to that of Fig. 5(a). From these results it follows that even by doing the integration over the full acceptance cone up to $\Delta\theta=\pm 2°$ (Ref. 7) or $\Delta\theta=\pm 3°$ (present experiment) a considerable amount of off-normal emission from the Δ_2 band must be visible in the spectra and that the corresponding peak is expected at the position where the unexplained structure occurs in the experiment. In addition, the calculations show that this off-normal emission from the Δ_2 band couples to *s*-polarized light and not to *p*-polarized light. In summary, this means that the theory predicts the appearance of a spin-split structure due to off-normal-emission contributions from the Δ_2 band which agrees in all points with the behavior of the observed unexplained structure.

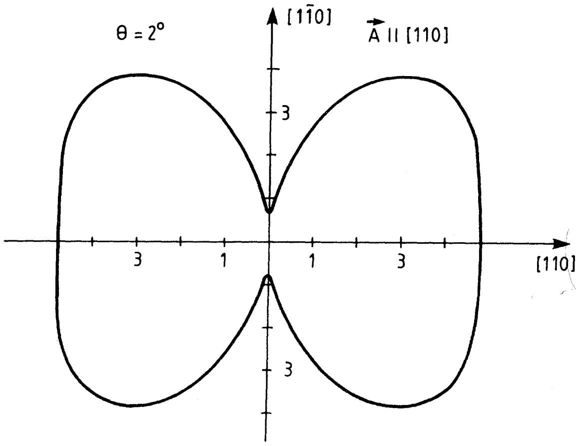

FIG. 6. Calculated azimuthal dependence of off-normal emission from Ni(001) for the special transition from a minority-spin initial state 0.25 eV below E_F with a photon energy of 21.22 eV. The polar angle is $\theta=2°$. The electric field vector is parallel to [110]. The emission intensity for a special angle is given in arbitrary units as radial distance from the origin.

In principle there is still the possibility of a structure of different symmetry appearing exactly at the same energy as the Δ_2 band emission. An example of such a case is shown in Fig. 2 in the work of Plummer and Eberhardt.[10] These authors find a surface state of $\bar{\Delta}_1$ symmetry close to E_F and near the $\bar{X}$ point of the SBZ and a non—surface-sensitive peak related to $\bar{\Delta}_2$ symmetry. In addition, near the $\bar{M}$ point of the SBZ they find a $\bar{\Sigma}_2$ surface state and a non—surface-sensitive peak related to $\bar{\Sigma}_1$ symmetry. It is interesting that for both directions the symmetries of the non—surface-sensitive structure are compatible with those of the Δ_2 band at $\bar{\Gamma}$ and also that Plummer and Eberhardt observed no dispersion with $k_\perp$ for this structure. Together with the known small dispersion of the Δ_2 band, especially if self-energy corrections are included, this might be a hint that off-normal emission from the Δ_2 band seems to show no dispersion with $h\nu$.

We have checked the surface sensitivity of the controversial spectral feature by investigating the influence of adsorption of oxygen up to exposures of 100 L (1 L$=10^{-6}$ Torr sec) on the spin-unresolved EDC. No important change of the considered structure was detected. In contrast to this result, Plummer and Eberhardt[10] report that their normal emission spectra are sensitive to adsorption of sulfur. But their energy resolution (0.3—0.4 eV) is obviously too low to resolve the shoulder which is clearly visible in the present polarized spectra and in the spectra of Erskine.[7] Additionally they find that the surface-sensitive structure moves with $h\nu$, contradicting the explanation as a surface structure. From all these results we conclude that this main structure in the normal-emission He I spectra which leads to the observed shoulder in the spin-unresolved EDC is neither a Δ_5 surface state (as claimed by Erskine[7]) nor a Δ_1 surface resonance (as assumed by Jepsen *et al.*[2]), but most likely the off-normal-emission contribution from the Δ_2 band.

We finally note that by more carefully analyzing our majority-spin EDC's we find that within the limits of the statistical error bars there may be an additional structure located even closer to E_F than the one which we ascribe to off-normal emission. Since this structure seems to appear in each one of the measured spectra it is possible that it is more than a statistical fluctuation. The structure is indeed too weak to be resolved in the conventional EDC or to be of major importance to the shoulder observed in the spectra. It does not seem to increase in intensity with the degree of p polarization of the light and so should be related to Δ_5 or Δ_2 symmetry. We cannot exclude that it belongs to the claimed surface state which can then be observed by approaching the $\bar{X}$ or $\bar{M}$ point of the SBZ. We note, however, that the calculated off-normal-emission spectra also show some very weak structures at this initial-state energy which even increase for larger polar angles. These structures are related to emission into the $\Delta_{2'}$ final-state band. To the question of the existence of a Δ_5 majority-spin surface state it should be remembered that such a state is not found in the self-consistent thin-film calculations of Jepsen *et al.*,[2] although this group identifies the observed magnetic $\bar{\Sigma}_2$ surface-state band near $\bar{M}$ (Ref. 10). The expectation of a strong Δ_5 majority-spin surface state is mainly based on the parametrized thin-film calculation of Dempsey and Kleinman[8] in which surface-parameter shifts were introduced to produce this surface state in order to explain the abrupt sign reversal of the measured electron spin polarization near emission threshold.[9] In later studies[16,17] it was shown that the sign reversal appears already without introducing such a surface state. The existence of a Δ_5 surface state is also found in the self-consistent thin-film calculation of Krakauer *et al.*[4] In addition these authors identify the observed surface structure near $\bar{M}$ as a $\bar{\Sigma}_2$ surface *resonance* and find the Δ_5 surface state not sufficiently localized in the surface layers to account for the sign reversal of the spin polarization. Krakauer *et al.* argue that the lack of observation of this state by Plummer and Eberhardt[10] is consistent with the very diffuse nature of this state.

IV. CONCLUSION

We have performed spin-polarized angle- and energy-resolved photoemission experiments to investigate the dependence on spin, polar angle, s and p polarization of the light, and on adsorbates of a controversial structure in the He I normal-emission spectra form Ni(001). This special feature was ascribed to the emission from a $\bar{\Gamma}_5$ ($=\Delta_5$) majority-spin surface state by Erskine[7] and to a Δ_1 surface resonance by Jepsen *et al.*[2] The Δ_5 majority-spin surface state was suggested by Dempsey and Kleinman[8] to be responsible for the spectral dependence of the spin polarization of the photoyield of Ni(001). From our new experimental results and their comparison with photoemission calculations we conclude that this controversial spectral feature can neither be related to emission from a Δ_5 surface state nor to a Δ_1 surface resonance. Instead we assign it to off-normal-emission contributions from the Δ_2 *minority*-spin band. Although emission from surface structures cannot be strictly excluded, it must be of very small intensity and therefore should not play an important role in the spectra. From the point of view of the new experimental technique of angle-resolved spin-polarized photoelectron spectroscopy the importance of off-normal-emission contributions found in this work indicates that an increased angular resolution (beyond the present $\Delta\theta=\pm3°$) is going to provide more information than a further increase in energy resolution.

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