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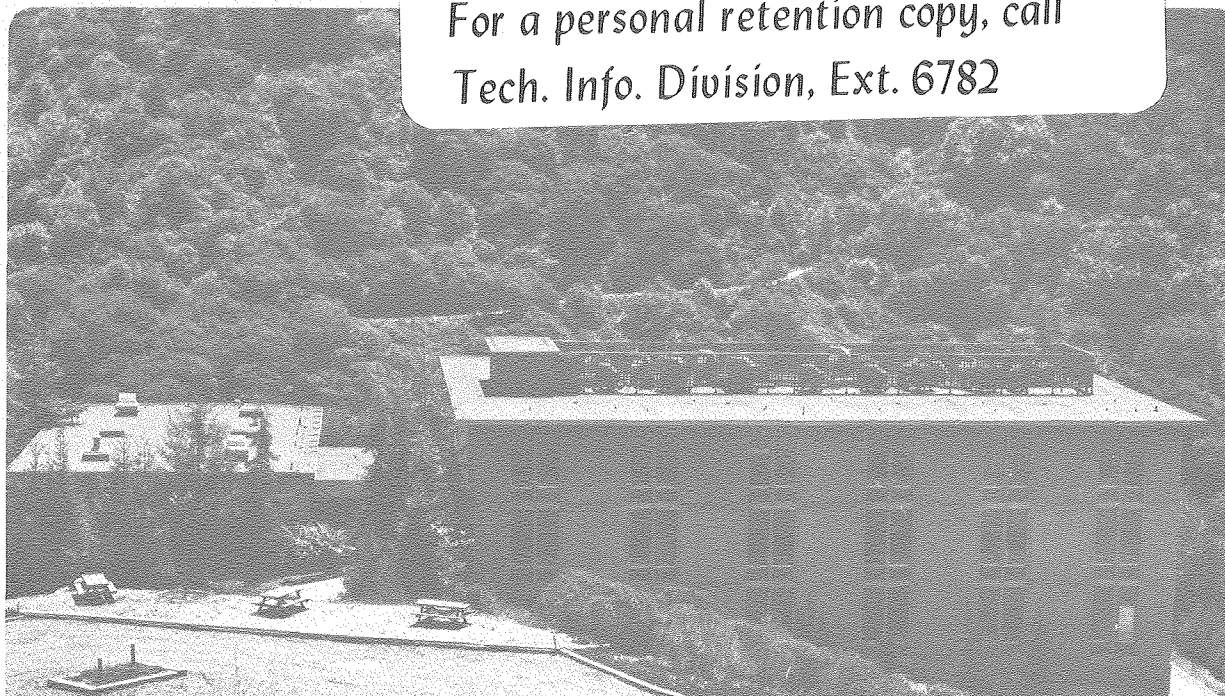## Materials & Molecular Research Division

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ABSTRACT

A large resonance was observed in the C(1s) angle-resolved photoemission cross-section of CO overlayers on Ni(111) and Ni(001), using synchrotron radiation at SSRL, while none was observed for O(1s). Energy-, angular-, and polarization-dependence measurements showed that the C(1s) resonance, which is peaked at $h\nu = 311$ eV, is closely related to the shape resonance predicted for the C(1s) level in isolated CO. However, the surface potential introduces strong substrate-dependent deviations from gas-phase theory.

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The study of the structure of molecular overlayers on metal surfaces by valence-band angle-resolved photoemission (ARP) has recently received considerable attention.[1] The primary result has usually been the determination of molecular axis $(\vec{M})$ orientation with respect to the crystal normal $(\vec{n})$, as inferred from comparison of experimental ARP intensities with gas-phase data and theory. Examples include the prototype systems CO-Ni(111)[2] and CO-Ni(001).[3,4] In the latter system, an intensity resonance in the overlayer level derived from the 4σ molecular orbital[4] has been assigned to the adsorbed-molecule analogue of the well-known gaseous CO valence-shell shape resonance.[5-7] It has been pointed out that the angular peaking of photoelectrons along the molecular axis at the shape resonance energy could serve as a direct "beacon" identifying the molecular adsorbate orientation,[6,8] provided that adsorbed molecules possess resonances similar to those predicted for free molecules.[6,9] In this connection, adsorbate core levels[9] possess distinct advantages for orientation studies, because their spatial localization eliminates ambiguities due to initial-state substrate effects.[10] In this Letter, we report the first observation of adsorbate core-level ARP resonances, for the C(1s) level in CO-Ni(111) and CO-Ni(001). Although these resonances are similar to the predicted oriented-molecule shape resonance,[8] there is strong evidence for both substrate perturbations and substrate specificity.

The ARP experiments employed soft x-rays from Beam line I-1 at the Stanford Synchrotron Radiation Laboratory, in the energy range 300 eV $\leq$ hν $\leq$ 360 eV. Our spectrometer, described elsewhere,[11] employs a 5.40-cm-mean-radius hemispherical analyzer with independent two-circle rotation. In these experiments, the relative orientations of the radiation vector potential ($\vec{A}$), the outgoing photoelectron direction ($\vec{p}$), and the crystal normal ($\vec{n}$) were independently varied in the plane of incidence. In this way, as shown in Fig. 1a, the emission angle $\theta_p = \angle(\vec{n},\vec{p})$ could be varied between 0° and 45° in the $\phi_p = 0°$ azimuth (toward the photon beam direction) and between 0° and 90° in the $\phi_p = 180°$ azimuth. The polarization angle $\theta_A = \angle(\vec{n},\vec{A})$ could be varied from 0° to 45° in the $\phi_A = 180°$ azimuth. The Ni(111) and (001) crystals had been cut and polished to within 1/2° of the [111] and [001] directions, respectively, etched, and cleaned in situ by cycles of ion bombardment and annealing. The azimuthal crystal orientations, shown in Fig. 1b, were held fixed throughout the experiments. Subsequent Auger analysis showed no surface impurities on Ni(111), but a post-anneal rapid cooling method similar to the one employed by Passler et. al.[12] was necessary to minimize carbon contamination of the Ni(001) surface prior to CO exposure. The 2L CO exposures and subsequent ARP measurements were made with the Ni(001) crystal cooled to 120K and the Ni(111) sample at 295K. The resulting LEED patterns were typically faint and diffuse, but showed ($\sqrt{3}$ x $\sqrt{3}$) R30° and c(2 x 2) structures for the (111) and (001) faces,

respectively. Normal emission C(1s) photoelectron diffraction studies of the same overlayers further characterized these sytems.[13] Complete photoemission energy distribution curves (EDCs) were collected at various photon energies, and relative C(1s) intensities were obtained as peak areas normalized to incident photon flux and analyzer efficiency.

The C(1s) resonance is clearly seen in Fig. 1c for normal emission from CO-Ni(111), where some of the normalized EDCs are plotted for a range of photon energies, sweeping through the resonance maximum at $h\nu$ = 311 eV. The total experimental C(1s) linewidth for photon energies in this region was 1.5 eV. This near-threshold ARP experiment was complicated by the large inelastic back-ground structure characteristic of condensed phase photoemission spectra. However, by collecting digital data with good statistical accuracy over a large energy range for each spectrum, and careful least-squares fitting, we were able to derive very accurate peak intensities. In Fig. 2, we show a region of the energy-dependent cross-section curve for CO-Ni(111) obtained from the EDC peak areas, along with similar results for CO-Ni(001). To facilitate a comparison of the two curves, they have been normalized at the minimum region around $h\nu$ = 335 eV. This procedure is justified because this region is the only portion of the total C(1s) cross section curve obtained that is relatively free of photoelectron diffraction modulations.[13] It thus approximates the "atomic-like" background near 335 eV.

As a further test of this point, the resonance peak intensity was also normalized to an "average" curve drawn through the ARP results at higher photon energies, thereby averaging over the modulations arising from photoelectron diffraction. The results were consistent. The two curves in Fig. 2 are seen to be nearly identical in shape and resonance peak position at $h\nu = 311$ eV, but the intensity maximum relative to the "atomic" value is attenuated by a factor of two for CO-Ni(001) relative to CO-Ni(111).

The characterization of this resonant behavior is aided by the previous orientation studies discussed above,[2-4] which yielded $\vec{M} \parallel \vec{n}$ for CO overlayers on both substrates.[14] Consequently, we have determined that the resonance has properties very similar to those for the shape resonance predicted in the C(1s) cross section in gaseous CO. For an oriented molecule, the shape-resonant photo-emission intensity should be sharply maximized in θ when the three vectors $\vec{A}$, $\vec{p}$, and $\vec{M}$ (or equivalently $\vec{n}$ in the present case) are aligned.[8] Figures 3a and b show that the adsorbate resonance has this property. In Fig. 3a, we show the θ_A-dependence of the near-resonance cross section for CO-Ni(111). In these measurements, $\vec{p}$ is fixed along $\vec{n}$, and the intensity is seen to increase as $\vec{A}$ is brought into near alignment with these two vectors. The θ_p-dependence of the C(1s) intensity at $h\nu = 311$ eV is shown in Fig. 3b for both systems. As $\vec{p}$ is brought to near alignment with fixed $\vec{n}$ and $\vec{A}$, the intensity reaches a maximum for CO on both substrates. Changes in

θ_p by 20° bring about intensity modulations by factors of 2 or more.

However, comparison of the resonant behavior for CO-Ni(111) and CO-Ni(001) allows us to identify several important differences between the predicted gas-phase and observed adsorbed-molecule shape resonances. These constitute substrate or condensed-phase effects, and are summarized below:

(1) The resonance intensity difference of a factor of two between the two nickel faces obviously cannot be accounted for by any isolated molecule theory,[8] and must indicate a strong substrate effect. A difficulty in this interpretation is that a substrate-induced attenuation of the shape resonance intensity _might_ also shift the energy of the resonance, contrary to our observation. A likely contribution to this intensity difference is the difference in adsorption-site geometries. Based on our photoelectron diffraction studies,[13] and LEED,[15] ELS,[16] and IR[17] measurements by other workers, CO is known to occupy the atop site on Ni(001) whereas the two-fold bridge site is occupied on Ni(111).

(2) For CO-Ni(001), the θ_p angular distribution shown in Fig. 3b is peaked at 5° in the $\phi_p = 180°$ azimuthal direction, exactly between the orientations of $\vec{A}$ and $\vec{M}$. Assuming that the dipole nature of the photoemission transition and the angular symmetry of the shape resonance are equally important in determining the resonant intensity maximum for the oriented molecule, this is exactly in agreement with theoretical predictions for isolated CO.[8] However,

the CO-Ni(111) distribution in Fig. 3b is peaked at 5° in the $\phi_p = 0°$ azimuth, and the entire curve is shifted by 10° in θ_p relative to CO-Ni(001), in a direction away from $\vec{A}$. This unexpected result for CO-Ni(111) is consistent with a substrate-induced shift of the ARP intensity maximum away from the molecular axis $\vec{M}$ (and thus from $\vec{n}$). We note that rotations of $\vec{p}$ by 180° about $\vec{n}$ are crystallographically equivalent for Ni(001) but not for the three-fold symmetric [111] axis on Ni(111). Hence, a substrate-induced shift of the angular distribution could be "symmetry-masked" in the ensemble for Ni(001) but not for Ni(111).

(3) For the adsorbate resonance, the vacuum-referenced resonance kinetic energy is shifted upward by 10 eV to 21 eV and the photon energy by 4 eV to 311 eV relative to gas phase predictions.[9] Loubriel and Plummer[18] have shown that shifts such as these are caused by potential changes upon bonding to the substrate. A differential shift of the resonance level with respect for C(1s) induces changes in both the kinetic and photon energy at resonance, relative to the gas phase.

Finally, we did not observe a resonance in the O(1s) cross-section for CO on either substrate. This result is in agreement with the oriented-molecule theory of Wallace, et. al.,[8] after phase errors in their original work are accounted for:[19] the core-level-resonance intensity is predicted to be sharply peaked along $\vec{M}$ with the electron intensity maximum in the direction opposite to the photoemitting atom. Because the adsorbed CO molecule is oriented with the C-end toward

the substrate on both Ni surfaces,[2-4] only the C(1s) level should give rise to a resonance in our experiment.

In conclusion, we have observed large resonances in the near-threshold C(1s) photoemission cross section for CO-Ni(111) and CO-Ni(001). These resonances appear to be closely related to the so-called "shape resonances" observed in gaseous[7] and adsorbate[4] CO valence levels, and predicted for the core levels.[9] As expected,[8] the C(1s) core-level resonances appear to be highly sensitive to molecular orientation and photon energy. This should facilitate interesting molecular orientation experiments with different adsorbate molecules.

An important unanticipated result of this research is the pronounced difference in the C(1s) resonance between Ni(001) and Ni(111). This result implies that future theoretical treatments of adsorbate shape resonance phenomena must take into account the position of substrate atoms to facilitate a meaningful comparison with theory.

Acknowledgments

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Figure Captions

Figure 1.   (a) Experimental arrangement, showing typical plane-of-incidence orientations of the vector potential $\vec{A}$, the outgoing photoelectron direction $\vec{p}$, the crystal normal $\vec{n}$, and the incident photon beam direction $h\nu$. The photoemission angle θ_p is varied in either the $\phi = 0°$ (toward the photon beam) or 180° azimuth, while the polarization angle θ_A is confined to the $\phi = 180°$ azimuth. (b) Experimental orientation of the crystals. In addition to the normal vector, the plane of incidence contains the [100] and [$\bar{2}$11] direction for the (001) and (111) face, respectively, in the $\phi = 0°$ azimuth. (c) C(1s) photoemission energy distribution curves for Ni(111) + 2L CO, with photons in the energy region near the resonance at $h\nu = 311$ eV. The spectra are normalized to incident radiation flux and analyzer transmission. θ_p and θ_A are defined in (a).

Figure 2.   Relative C(1s) photoemission cross section for CO-Ni(111) [solid line] and CO-Ni(001) [dashed line] in the energy region 300 eV $\leqslant h\nu \leqslant$ 356 eV. The two curves are normalized to each other at $h\nu = 335$ eV, and the resonance maximum for both curves is shown to lie at $h\nu = 311$ eV. θ_p and θ_A are defined in Fig. 1a.

Figure 3. Relative C(1s) cross section: (a) θ_A-dependence in the energy region near the resonance maximum for CO-Ni(111) and various values of the polarization angle. (b) θ_p-dependence at $h\nu = 311$ eV, with the polar orientation of $\vec{p}$ varied in both the 0° and 180° azimuths about the crystal normal in the plane of incidence. Data are shown for both CO-Ni(111) [closed circles, solid line] and CO-Ni(001) [open circles, dashed line], where the CO-Ni(001) curve has been normalized so that its value at $\theta_p = 0°$ equals the corresponding value for CO-Ni(111). θ_p, θ_A, and ϕ_p are defined in Fig. 1a.
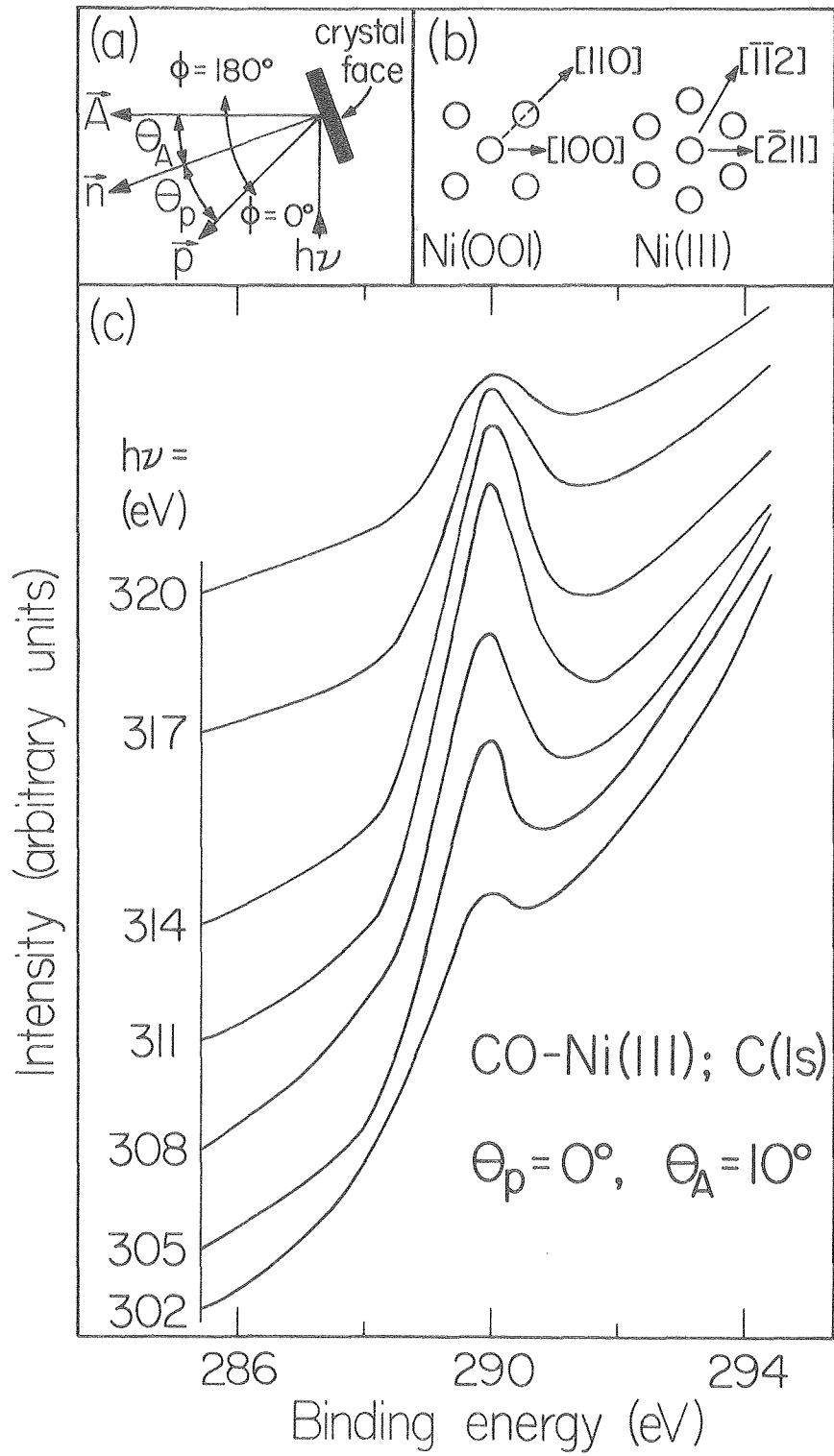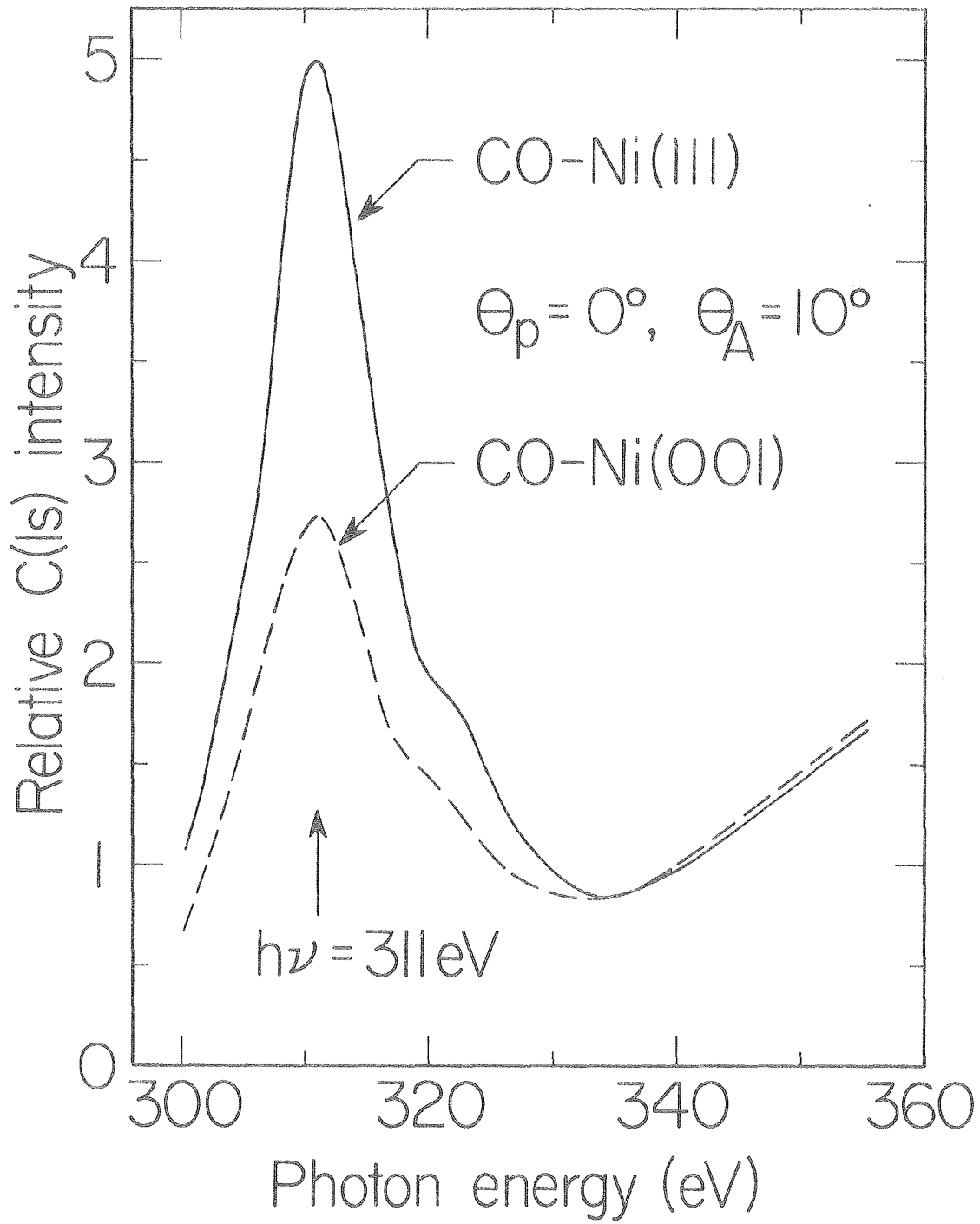
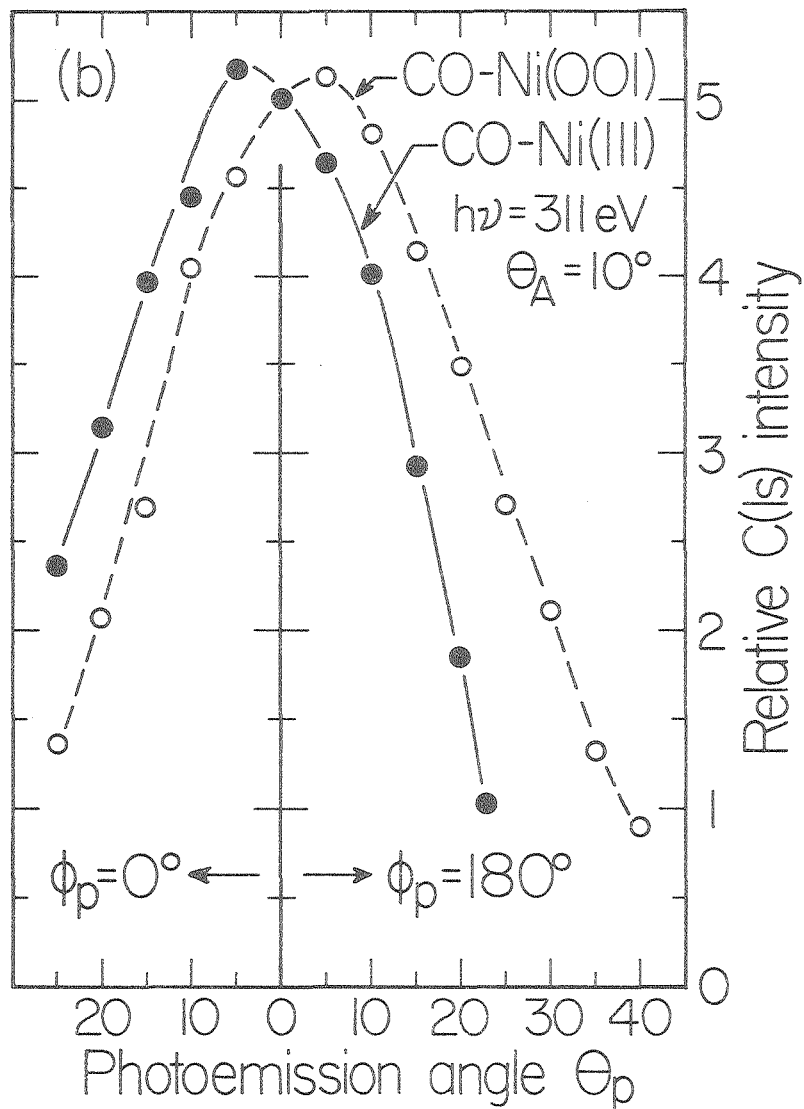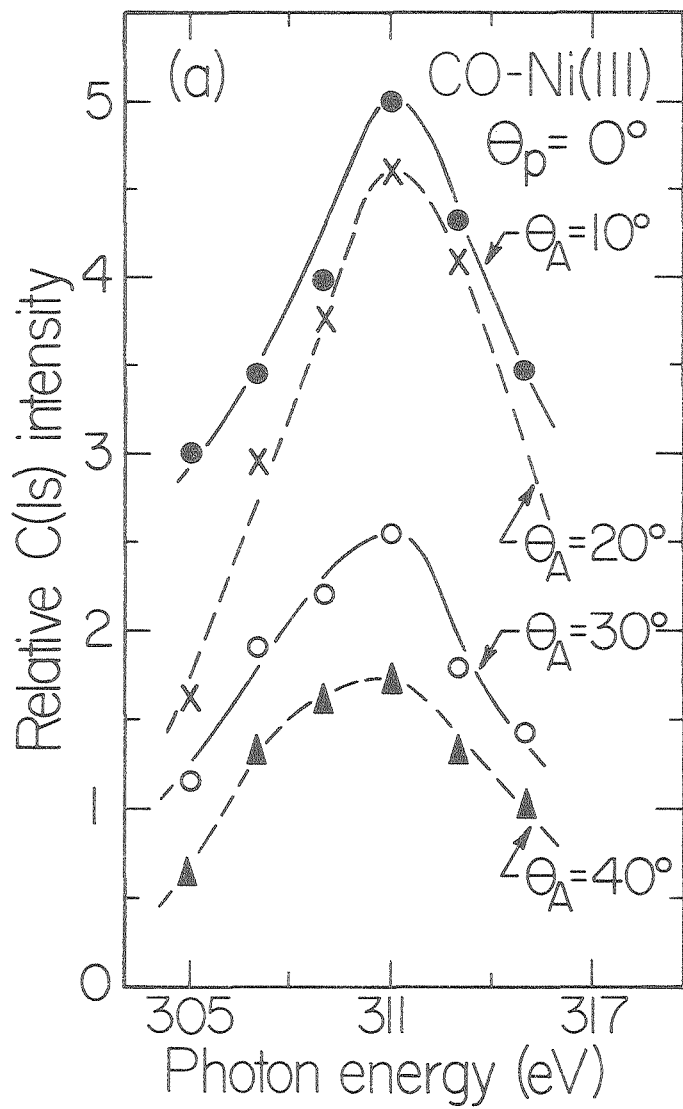Fig. 1   XBL 808-11120

Fig. 2

XBL 808-11119

Fig. 3

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