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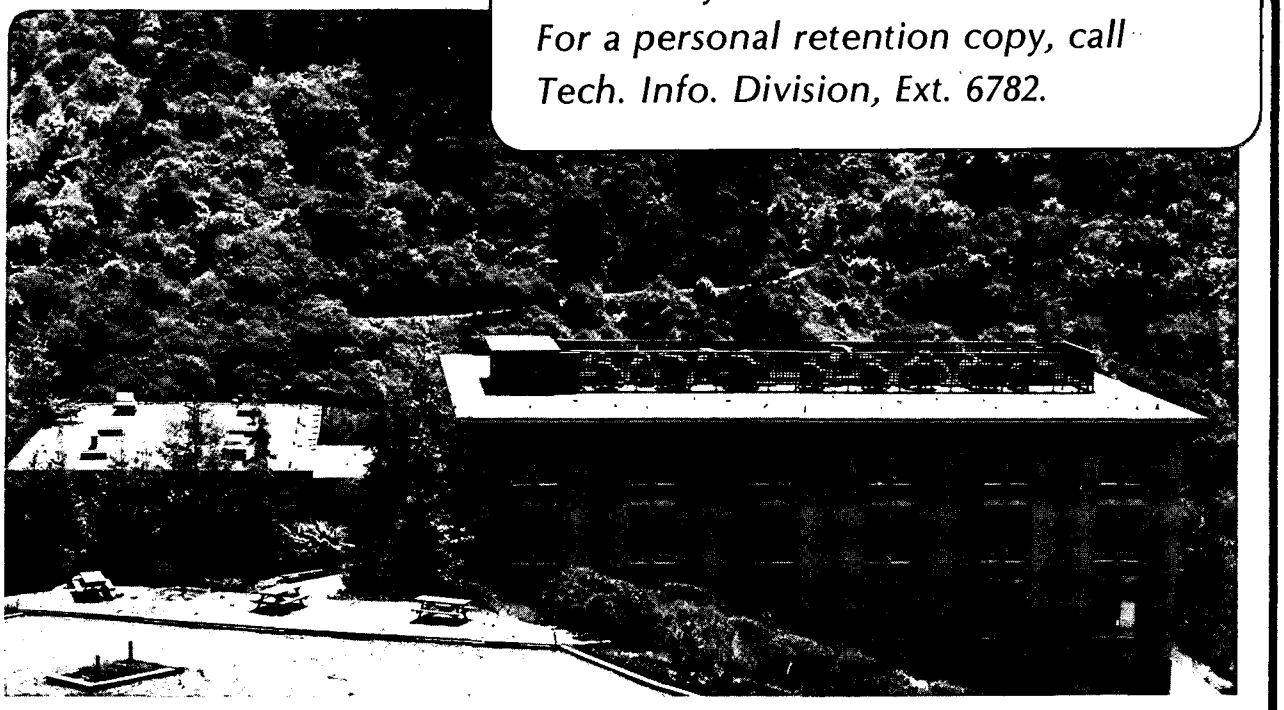

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Observation of a Surface Magnetic Phase Transition on Cr(100)

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ABSTRACT

We have observed a surface magnetic phase transition on Cr(100) using Angle-Resolved Photoelectron Spectroscopy (ARPES). The temperature dependence of a surface resonance indicates a transition temperature of 780 ± 50 K. This is consistent with theoretical predictions of a ferromagnetic Cr(100) surface. The room temperature ferromagnetic surface exchange potential is estimated to be 0.8 ± 0.1 eV, with an associated surface magnetic moment of $2.4 \pm 0.3\mu_B$.

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Transition metals have been the "proving ground" of the latest theoretical attempts to predict the behavior of electrons at surfaces.[1,2] One aspect of this behavior is surface magnetism. Many experiments have investigated the differences in magnetic properties between the surface and bulk atoms of ferromagnets.[3-5] However, a most extraordinary manifestation of surface magnetism would be the postulated existence of surface ferromagnetism on an otherwise antiferromagnetic chromium crystal.[6-8] Photoemission evidence for this possibility is the subject of this Rapid Communication.

The surface magnetic properties of Cr(100) have received the greatest theoretical interest.[6-8] The relatively few (4) nearest-neighbors for the (100) surface atoms leads to energy band narrowing, resulting in the formation of large, localized surface magnetic moments. Allan's self-consistent tight-binding calculation[6] for Cr(100) predicted a ferromagnetic surface phase characterized by an exchange-split surface spin density of states (SSDOS), and large ($2.8\mu_B$) localized magnetic moments. Grempel[7] confirmed these results and extended the calculation to finite temperature using spin-fluctuation theory. His results predicted the persistence of surface ferromagnetic order up to 850 K, well above the bulk Néel temperature of 312 K.

Prior to this year, most experimental studies of chromium surfaces have been plagued by surface contamination problems. Meier et al.[9] found zero spin polarization of electrons photoemitted from a Cr(100) surface. They concluded that no ferromagnetism was present

for an oxygen-free surface. However, their sample was contaminated with as much as one monolayer of nitrogen. Celotta et al.[3] have shown that submonolayer surface contamination can greatly reduce surface magnetism. Consequently, the work of Meier may be irrelevant to the question of ferromagnetism on clean Cr(100). Raue[4] used one-electron capture (OEC) spectroscopy to study the spin polarization of electrons at the Cr(100) surface. He and his co-workers found evidence of long-range ferromagnetic order at the surface below 365 K. However, their sample displayed the c(2x2) Low Energy Electron Diffraction (LEED) pattern indicative of carbon, oxygen or nitrogen impurities. How these impurities affected the results is not known. Recently, Gewinner et al.[10] reported a surface state in their Angle Resolved Photoelectron Spectroscopy (ARPES) study of bulk Cr(100) electronic structure. The relationship between this surface feature and the possible existence of surface ferromagnetism was not explored.

We present here an ARPES investigation of a truly clean Cr(100) surface that reveals a surface magnetic phase transition near 780 K. A surface-related photoemission feature is shown to display a dramatic temperature dependence, in contrast to bulk antiferromagnetic states.[11] The results are discussed within the existing theoretical framework.[6,8]

The experiment was conducted on Beam Line I-I of the Stanford Synchrotron Radiation Laboratory using our Angle-Resolved Photoelectron Spectrometer[12]. As in a previous study[13], the sample was Argon ion bombarded with high temperature (1120 K) cycling for three weeks to remove bulk nitrogen as detected by Auger Electron

Spectroscopy (AES). The crystal then displayed a very sharp, low background, 1X1 LEED pattern. No impurities were detectable by AES, or more sensitively, by ARPES.[14] Temperature-dependent spectra were measured by flashing the crystal to 1120 K, turning off the heater, and taking quick ARPES scans during well-defined temperature intervals on the cooldown curve. All reported spectra were collected using 23 eV photon energy.

Figure 1 compares room temperature normal emission ARPES spectra of clean Cr(100) and Cr(100) exposed to 5L of CO.[15] All binding energies are referenced to the Fermi level, E_F. Note the sharp attenuation of those features with binding energies of 0.16 eV (referred to hereafter as feature 1) and 0.75 eV (assigned to a surface state in ref. 10., hereafter referred to as feature 2). Figures 2-4 reveal different characteristics for the two features 1 and 2. In Fig. 2, peak 2 shows strong suppression and binding energy dispersion in off-normal emission. This is typical of a surface state or resonance with well-defined orbital character.[16] We tentatively assign feature 2 to a surface resonance.[17] In contrast, there is little evidence that 1 is a surface state or resonance. The binding energies of 1 and 2 obtained[18] from spectra like those in Fig. 3 are plotted against temperature in Fig. 4. Clearly, the thermal modification of 2 is larger in magnitude and different in character than that of 1.

These observations have an interpretation within existing theory.[6,8] Allan's ferromagnetic solution for the Cr(100) surface

phase employs a self-consistent surface potential with two components. The first, V_o, is a single intra-atomic matrix element that approximates the potential produced by surface charge oscillations.[6] V_o is calculated to be 0.6 eV (E_F = .53 eV).[6] The second component, $V_s^{\mp}$, is the spin-dependent exchange potential:

$$V_s^{\mp} = \pm J\delta n_s \qquad (1)$$

J is the exchange constant (assumed equal to the theoretical bulk value, 0.67 eV) and $2\delta n_s$ (e.g. $2\delta n_s = \delta n_s^+ - \delta n_s^-$) is the surface magnetic moment M_s, in units of the Bohr magneton. Allan obtained values of ~ 0.9 eV for V_s and ~ $2.8\mu_B$ for M_s. Both SSDOS shift with V_o. The majority (+) and minority (-) SSDOS are then shifted about V_o by $-V_s$ and $+V_s$, respectively.[6] Figure 5 reproduces these SSDOS from Fig. 4 of Ref. 6. Note the peak labelled A in the occupied majority SSDOS. Its binding energy (with respect to E_F) is very near $(V_s + E_F - V_o)$.[6] .

We believe that the surface resonance 2, with binding energy 0.75 eV, can be associated with the peak A in the theoretical majority SSDOS of Fig. 5. We assign feature 1 to a peak produced by the truncation of the rise in the minority SSDOS by the Fermi level. Thus 2 has predominantly majority spin character; 1 mostly minority spin character. These assignments explain most of the experimental facts. Since both 1 and 2 are surface related, they are sensitive to contamination as displayed in Fig. 1. Since 2 is a surface resonance, its dispersion and strong intensity variation shown in Fig. 2 are not

surprising. However, 1 is a manifestation of a rise in the minority SSDOS and should not a priori be expected to show such behavior.

The temperature dependence of the binding energies plotted in Fig. 4 cannot be attributed to a structural modification of the surface, since a 1X1 LEED pattern was observed throughout the temperature range. Chemical contamination can be excluded from the ARPES data.[14] The temperature independence of bulk antiferromagnetic features[11] precludes the assignment of the phenomenon depicted in Fig. 4 to a bulk magnetic transition. The behavior in Fig. 4 can only be explained as a surface magnetic phase transition.

A surface magnetic phase transition would involve a thermally induced reduction of the surface exchange potential V_s. If feature 2 is a peak in the occupied majority SSDOS, then its binding energy should decrease proportionately with V_s. To test this hypothesis, we have scaled and graphed in Fig. 4 the temperature-dependent bulk exchange splitting in nickel Δ_{ex}^{Ni}, as measured by ARPES.[19] The binding energy of feature 2 is seen to decrease with temperature in a manner very similar to that of a ferromagnetic exchange splitting. It also grossly resembles the temperature-dependent total Cr(100) surface magnetization as calculated by Grempel.[7] However, Grempel's spin-fluctuation calculation predicts only a 10 percent decrease in the surface local band exchange splitting with increasing temperature. Our results do not support this prediction.

Nickel is a ferromagnet with known Curie temperature (T_c^{Ni} = 651 K). Consequently, the temperature dependence of feature 2's

binding energy can be compared with the form of $\Delta_{ex}^{Ni}(T)$ (as observed in ARPES[19]) to yield an estimate of the macroscopic Cr(100) surface magnetic phase transition temperature, T_s. From our data for feature 2 in Fig. 4, we estimate T_s to be 780 ± 50 K. This is near Grempel's prediction[7] of 850 K, and very close to the surface magnetic transition temperature (800 K) observed in macroscopic magnetization measurements of small (380-750 Å dia.) bcc chromium particles.[20]

Recall that feature 1 is not an occupied peak in the minority SSDOS but is rather a peaked spectral profile resulting from the occupation of the minority SSDOS with a Fermi-Dirac distribution. The location of this "peak" would not be expected to give direct information about V_s because it would be relatively insensitive to a shift in the minority SSDOS accompanying a reduction of the surface magnetization. This is generally the behavior of 1 in Fig. 4.

Both the commensurability of the existing theory[6,8] with the experimental facts, and the resemblance of feature 2's temperature dependence to ferromagnetic behavior indicate that the Cr(100) surface is in fact ferromagnetic. We now estimate room temperature ferromagnetic surface quantities. Assuming that feature 2 is a majority SSDOS peak with a binding energy of $(V_s + E_F - V_o)$, we obtain a surface ferromagnetic exchange splitting V_s of 0.8 ± 0.1 eV. From equation (1) and assuming J = .67 eV, the surface magnetic moment M_s is estimated to be $2.4 \pm 0.3\mu_B$, much larger than the maximum bulk value of $0.59\mu_B$.[21] These values are in good agreement with the

values $V_s \sim 0.9$ eV and $M_s \sim 2.8\mu_B$ predicted by Allan.[6]

In conclusion, we have observed a surface magnetic phase transition on Cr(100) at 780 ± 50 K. The assignment of the surface feature 1 to the minority SSDOS and feature 2 to a majority spin surface resonance accounts for their surface sensitivity and differing character in off-normal ARPES. The theory of Allan[6,8] and a previous ARPES investigation[19] of ferromagnetic nickel explain the temperature dependence of these features: it is a manifestation of the thermal decrease in the exchange potential V_s of a ferromagnetic Cr(100) surface. The room temperature surface exchange potential was estimated to be 0.8 ± 0.1 eV, with a surface magnetic moment value of $2.4 \pm 0.3\mu_B$.

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14. The presence of an oxygen 2p photoelectron peak at 6.7 eV binding energy is a sensitive indication of surface contamination by carbon monoxide decomposition. See Fig. 1.
15. Saturation coverage is achieved at 1L exposure; A.G. Baca, private communication.

16. Shang-Lin Weng, E.W. Plummer, and T. Gustafsson, Phys. Rev. B 18, 1718 (1978).

17. A complete discussion of the spectroscopic evidence for this assignment is in preparation.

18. Least-squares fits of the spectra employed a Gaussian broadened step function for the bulk background, and a Gaussian for feature 2. The true spectral profile of 1 is a priori unknown (see text). We used a Lorentzian in the fits to determine the "peak" binding energy of feature 1. The highest temperature spectrum was not fit well by this two peak model. For this temperature we report in Fig. 4 the binding energy of a single Gaussian fit to the spectrum.

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FIGURE CAPTIONS

FIG. 1. Normal emission Cr(100) ARPES spectra before (line) and after (dots) 5L CO exposure.

FIG. 2. (Line): Normal emission ARPES spectrum; (Dots): spectrum taken with the electron analyzer moved 5° away from normal in the [010] mirror plane.

FIG. 3. The effect of temperature on the normal emission ARPES spectrum.

FIG. 4. The binding energies of the surface features 1 and 2 plotted vs. temperature. The solid line is the temperature dependence of the bulk exchange splitting in nickel as measured by ARPES. This curve, reproduced from Fig. 2 of Ref. 19 and scaled in energy to our figure, should only be compared with the temperature dependence of feature 2.

FIG. 5. Theoretical Cr(100) majority SSDOS (solid line) and minority SSDOS (dashed line), reproduced from Fig. 4 of Ref. 6. States to the left of E_F (0.53 eV) are occupied. Recall that V_0 = 0.6 eV.

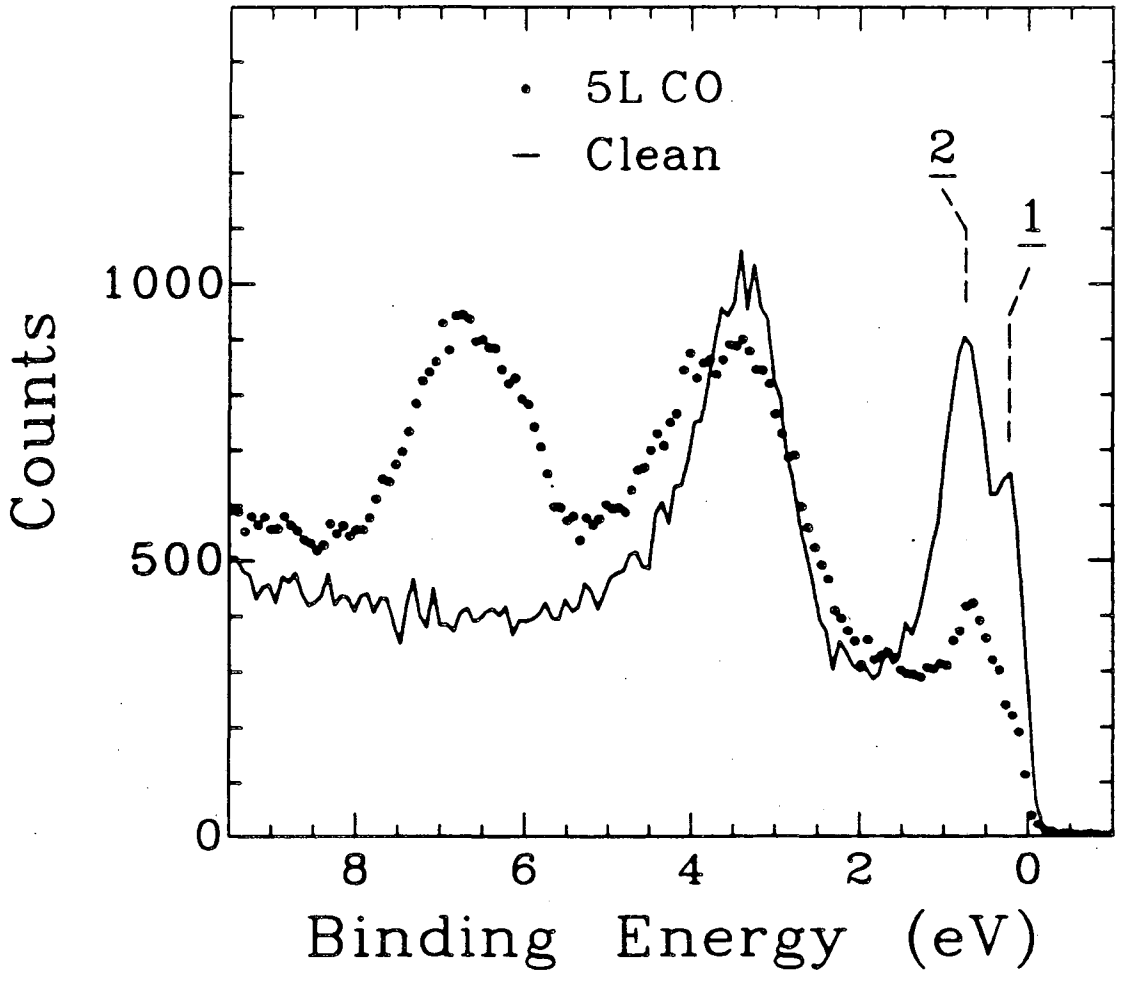

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Figure 1

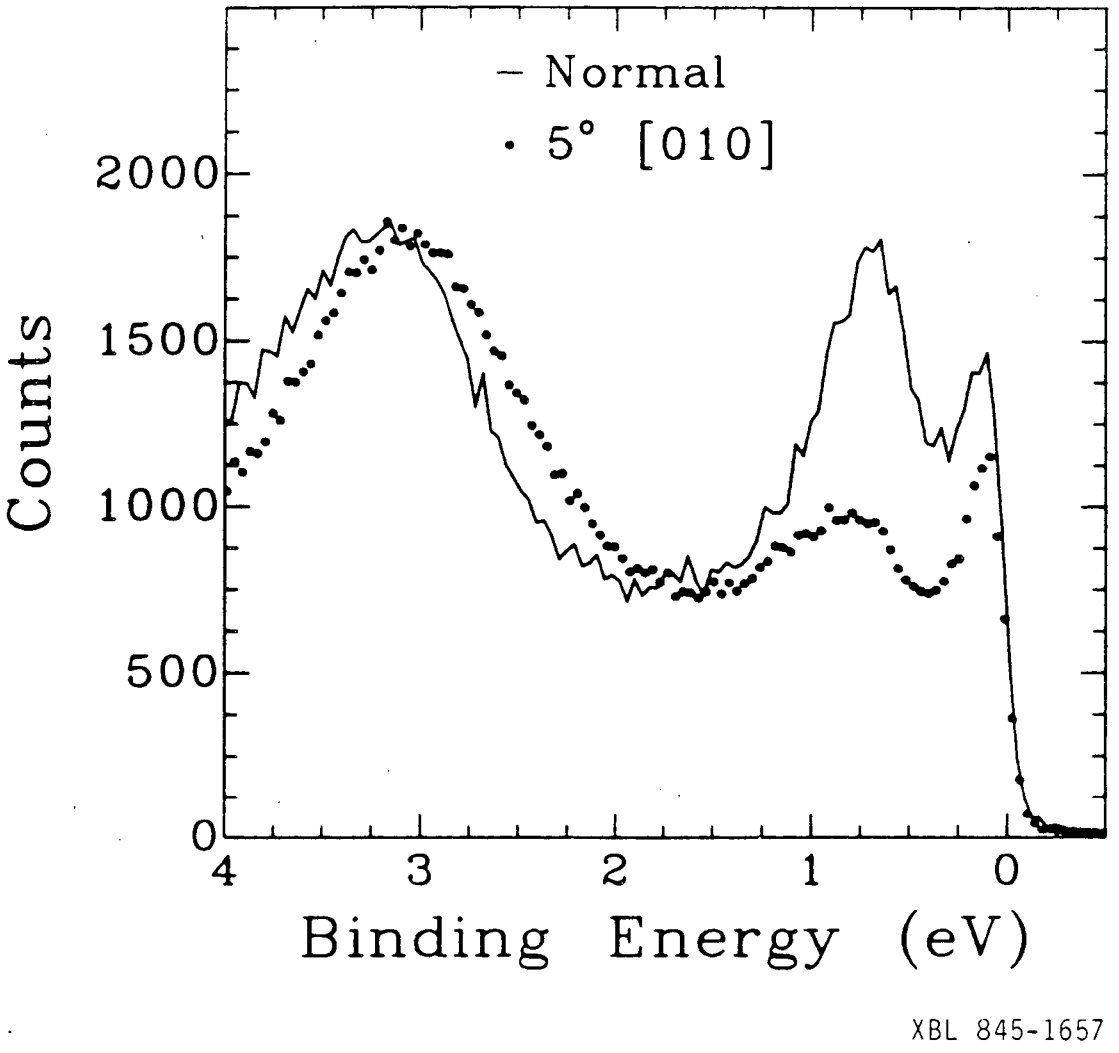

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Figure 2

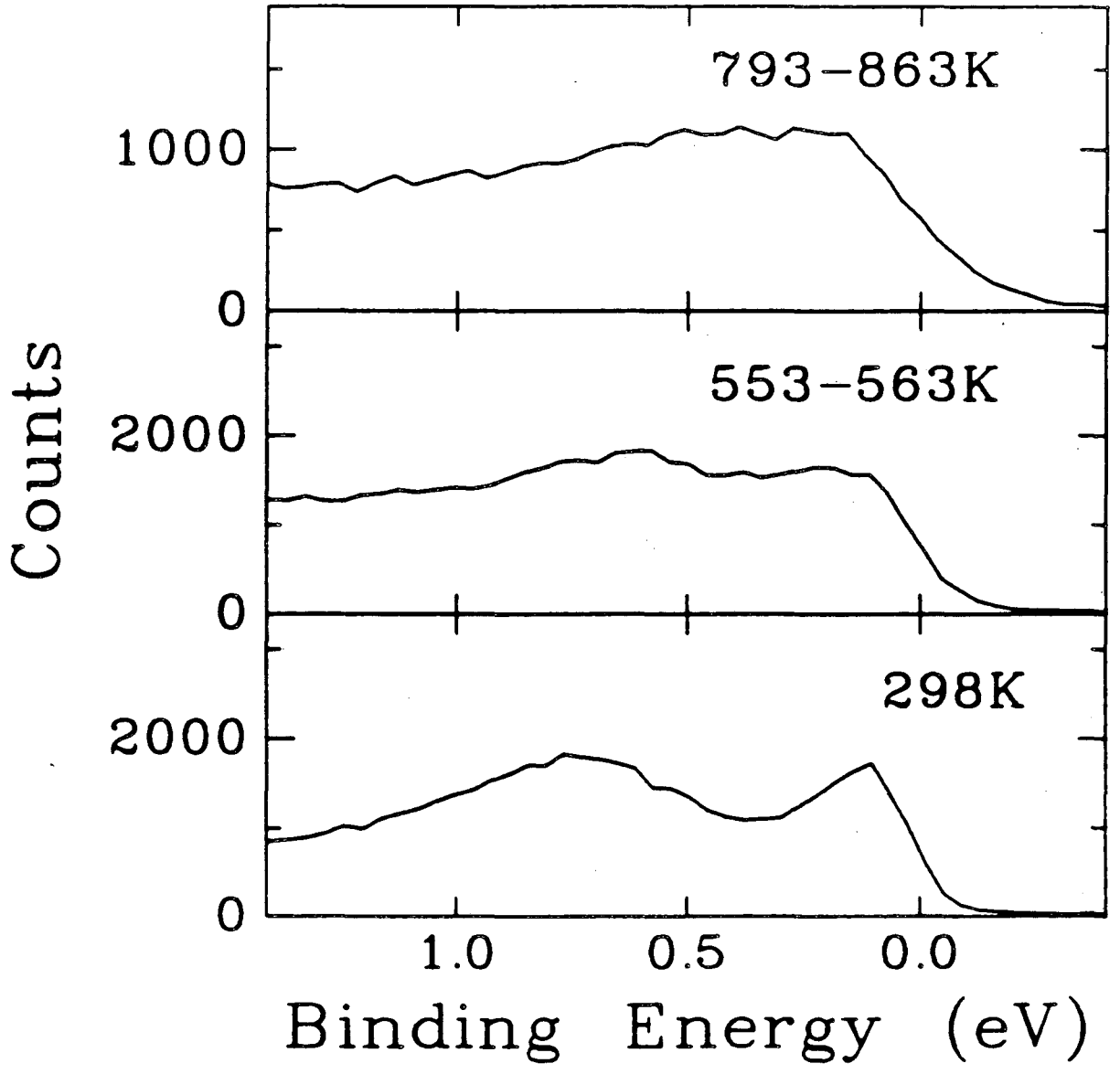

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Figure 3

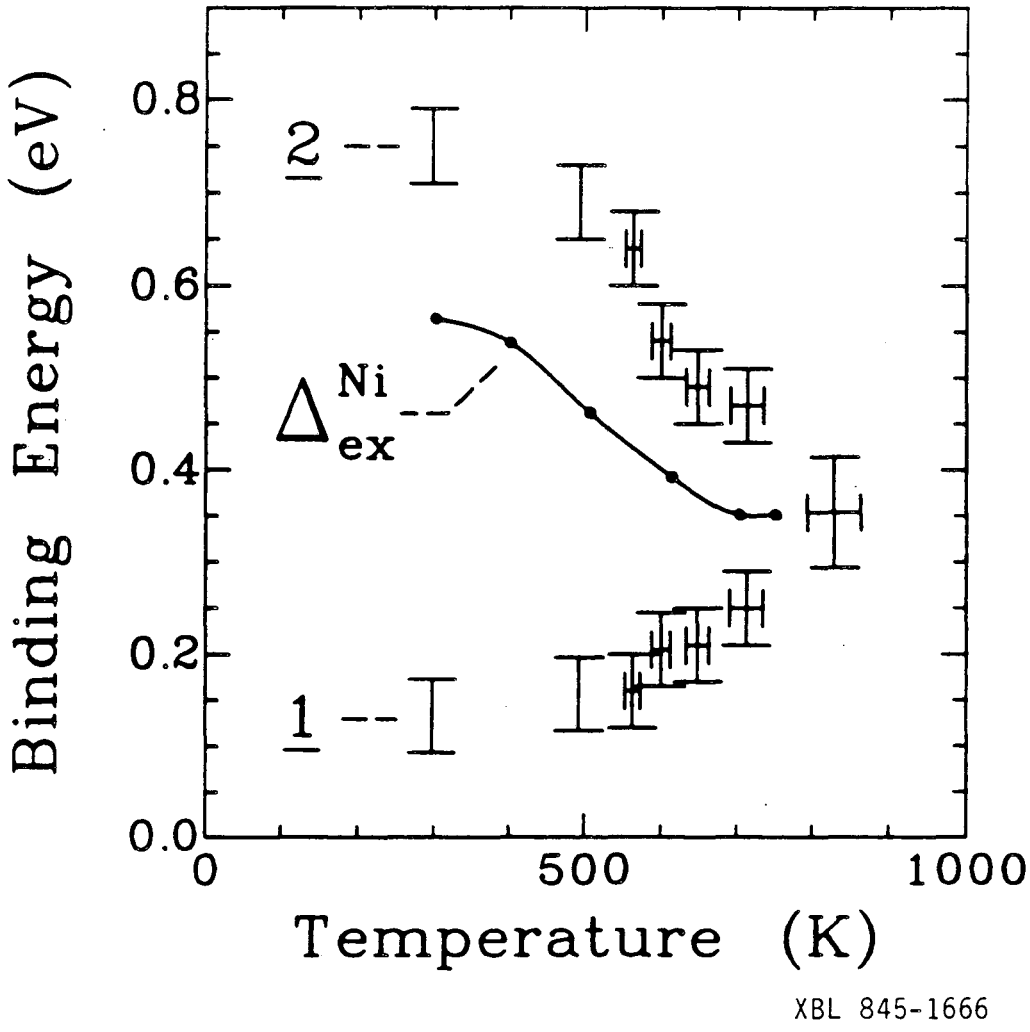
Binding Energy (eV)
0.0
0.2
0.4
0.6
0.8
0
500
1000
Temperature (K)
2
1
Δ_{ex}^{Ni}
XBL 845-1666

Figure 4

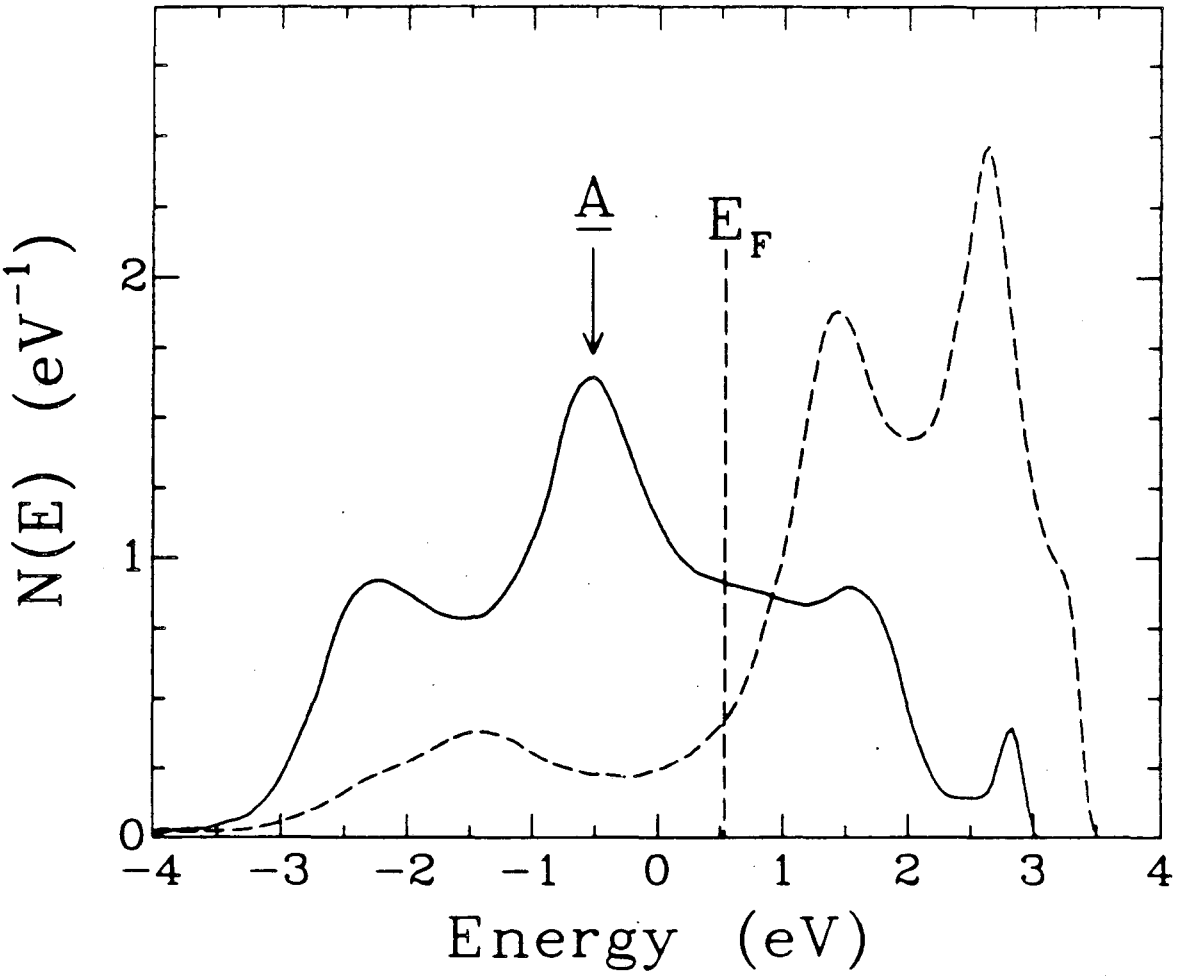

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Figure 5

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