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# Persistence of the Au(100)-(1 × 1) $\overline{M}_3$ surface state at the Cr/Au(100) interface: Epitaxial growth of a gold-chromium alloy

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The evolution of the Au(100)-(1×1) Tamm surface state with $\overline{M}_3$ symmetry upon deposition of Cr in the range 0–4 monolayers (ML) is studied by angle-resolved photoelectron spectroscopy and low-energy electron diffraction. Deposition of a small amount of Cr (~0.3 ML) on room-temperature clean Au(100)-(5×20) quickly converts the reconstructed surface to Au(100)-(1×1) with the concomitant $\overline{M}_3$ surface-state emission. With increasing Cr coverage the surface state progressively shifts from 1.6 to 2.7 eV binding energy, decreases in intensity, and eventually vanishes near 2 ML. When the substrate temperature is held at 400 K or higher during evaporation, the surface state even subsists up to coverages as high as 3 ML with an intensity comparable to clean Au(100)-(1×1). We present photoemission data from coevaporated Au-Cr alloys as well as oxidation experiments that demonstrate that this remarkable behavior is the result of surface intermetallic alloy formation. Actually it is found that the first 2 or 3 ML of Cr, deposited on Au(100) at room temperature or above, in-diffuse and occupy Au lattice sites forming an epitaxial substitutional $Au_{1-x}Cr_x$ ($x \leq 0.5$) alloy. The latter exhibits a Au-rich surface with Au(100)-(1×1) patches covering essentially the whole surface for substrates held at 500 K during evaporation, and the highly surface localized Au(100)-(1×1) $\overline{M}_3$ state, which is derived from in-plane Au $5d_{xy}$ orbitals, persists as a true surface state in a Au(100)-(1×1) monolayer supported on $Au_{1-x}Cr_x(100)$.

## I. INTRODUCTION

In recent years considerable work has been devoted to metal-metal interfaces and ultrathin metal overlayers because these systems offer the opportunity of observing many novel and intriguing properties.[1] Of particular interest is the possibility of epitaxial growth of well-ordered ultrathin transition-metal films on noble-metal substrates. In this respect, the Cr/Au(100) and Cr/Ag(100) appear to be good candidates because of the nearly perfect match of the 2D lattice translation vectors of Cr(100) and Au(100) or Ag(100). The evolution of the structural, electronic, and magnetic properties of the Cr overlayers versus film thickness is a central issue in the study of these systems. For instance, theory[2,3] predicts a strong enhancement of magnetism in ultrathin films of Cr, an element located on the borderline between magnetic and nonmagnetic metals of the 3*d* transition series. On the other hand, strong effects on the bulk electronic structure of Cr are expected as the film thickness is progressively reduced, such as *d*-band narrowing or a discretization of the energy spectrum for a given $k_{\parallel}$, the component of momentum parallel to the surface. In a recent paper we demonstrated that such effects are actually observed in ultrathin epitaxial bcc Cr films on Au(100).[4] Enhancement of magnetism, however, seems less important than predicted theoretically[2,3] for Cr on Ag(100) (Refs. 5 and 6) or Cr on Au(100).[4]

Still another interesting aspect of the formation of metal-metal interfaces, namely the behavior of the substrate surface states against metal overlayer adsorption, deserves a detailed investigation. In this respect, O'Neill and Weaver[7] recently reported the intriguing observation of the persistence of the Au(100)-(1×1) $\overline{M}_3$ surface state for Cr coverages as high as two monolayers (ML). These authors, assuming a sharp interface, interpreted their results in terms of an evolution of the surface state into an interface state. However, later on, we have shown[8] that the Cr/Au(100) interface is actually diffuse when formed at room temperature (RT) or above. At 400 K about 3 ML of Cr entered substitutionally into the fcc Au lattice and formed an interfacial epitaxial alloy. This led us to suggest an alternative explanation for the persistence of the Au(100)-(1×1) $\overline{M}_3$ surface state upon Cr deposition, in terms of gold segregation at the surface of the epitaxial $Au_{1-x}Cr_x$ alloy. This results in a superficial Au(100)-(1×1) top layer with the concomitant $\overline{M}_3$ Tamm state, which is known to be very surface localized from previous studies.[9,10] In this paper we present photoemission measurements which demonstrate that the latter explanation is indeed the correct one.

## II. EXPERIMENTAL DETAILS

The experiments were carried out *in situ* in an ultrahigh vacuum chamber equipped with low-energy electron diffraction (LEED), angle-resolved ultraviolet photoemission spectroscopy (ARUPS), and x-ray photoemission spectroscopy (XPS) techniques. The angular and total-energy resolutions are typically 3° (15°) and 0.2 eV (1 eV), respectively in ARUPS (XPS). The single-crystal Au(100) substrate was mechanically and chemically polished and cleaned *in situ* by sputtering and annealing at ~800 K until the surface exhibited the characteristic

Au(100)-(5×20) reconstruction and no impurities were detectable by XPS. Various amounts of Cr in the 0–4-ML range were evaporated onto the substrate kept at temperatures between 300 and 500 K from a Cr source operating at a typical rate of 0.5 ML/min [1 ML equivalent to the surface density of Au(100)] and a pressure of $5\times10^{-10}$ Torr. Epitaxial $\mathrm{Au}_{1-x}\mathrm{Cr}_x$ alloys were also prepared by coevaporation of Au and Cr onto clean Au(100). The thickness was about 20 Å and the concentration $x$ was estimated either from the ratio of Au and Cr evaporation rates or from core-level intensity measurements. With the substrate temperature held at RT an excellent (100)-(1×1) LEED pattern was observed for $x \leq 0.5$. As shown in Ref. 4, a random substitutional epitaxial Au-Cr alloy can be formed in this way on Au(100).

## III. EFFECT OF Cr DEPOSITION ON THE Au(100)-(1×1) $\overline{M}_3$ SURFACE STATE

Figure 1 shows a series of angle-resolved photoemission spectroscopy (ARPES) spectra taken with a photon energy $\hbar\omega=21.2$ eV at a polar angle of emission $\theta=50°$ in the (010) plane of the fcc Au substrate for various Cr coverages of the surface held either at RT or 500 K during deposition. This collection geometry probes the $\overline{M}$ point of the Au(100)-(1×1) surface Brillouin zone. Let us first consider the spectra corresponding to clean Au(100)-(5×20) and Au(100)-(1×1) surfaces, respectively. The stable form of the surface is the (5×20) reconstructed overlayer. The (1×1) arrangement was prepared in a metastable form by $\mathrm{N}_2$-ion bombardment at 200 eV energy and 1 $\mu$A/cm$^2$ current density during ~30 min.[11] The relevant spectrum is in good agreement with the data of Ref. 11. The dominant structures in these spectra reflect emission from Au 5$d$ bands in the 2–9-eV binding-energy (BE) range. The feature of interest here is the peak at ~1.7 eV BE visible in the clean Au(100)-(1×1) spectrum in a region where only $sp$-like bulk states exist. The relevant initial state has been identified previously (Refs. 9–11) as a Tamm-surface state with $\overline{M}_3$ symmetry located above the Au 5d-bulk bands. Note that this surface state is derived from Au 5$d_{xy}$ orbitals split off from bulk $d$ bands by the surface potential. The state is characteristic of the (1×1) surface atomic arrangement and highly surface localized (Refs. 9–11).

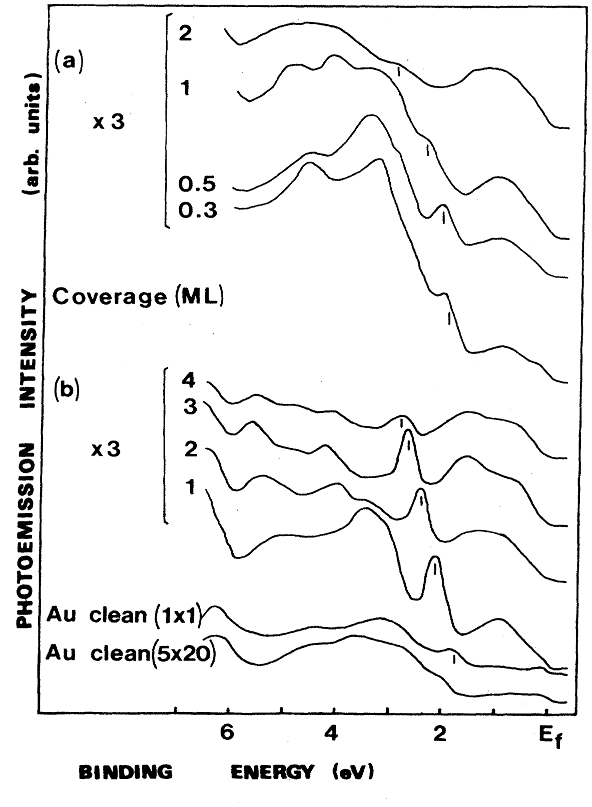

FIG. 1. Evolution of the Au(100)-(1×1) $\overline{M}_3$ surface state upon Cr deposition onto Au(100) held at (a) room temperature and (b) 480 K. The photon energy is 21.2 eV and the polar angle of emission $\theta=50°$ in the (010) plane.

When the substrate is kept at room temperature, deposition of an amount of Cr as small as 0.3 ML quickly converts the reconstructed (5×20) surface to (1×1) as judged by LEED. This means that the (1×1) surface can be stabilized by a small amount of Cr. As can be seen in Fig. 1 this is accompanied by the appearance of a peak which exhibits all the properties of the $\overline{M}_3$ Tamm state described in Ref. 11, except the energy location which shows a BE shift of +0.1 eV with respect to clean Au(100)-(1×1), suggesting a high sensitivity of the state's energy to the changes in surface potential brought about by the Cr species, as expected for a Tamm surface state. The most surprising result, however, is that the surface state is not degraded by further Cr deposition. Actually, its intensity first shows little change in the 0.5–1-ML range, then decreases progressively and finally vanishes near 2 ML for the interface formed at RT. With the substrate held at 480 K during Cr deposition, the behavior is even more spectacular. The state's emission subsists up to 4 ML and its intensity remains quite constant in the 1–3 ML range and is approximately twice that observed on the interface prepared at RT or on clean Au(100)-(1×1) when prepared as indicated above. A remarkable difference with the RT data is also apparent at submonolayer coverages since, at 480 K (5×20) spots remain visible in the LEED pattern up to 1 ML. Since the surface state is also observed at coverages below 1 ML (1×1) and (5×20) patches must coexist on the surface for submonolayer Cr deposition on the substrate held at higher temperatures. As can be seen in Fig. 2, which summarizes all the intensity data versus Cr coverage and substrate temperature, an intermediate behavior is observed for deposition on a substrate at 400 K. It is important to note that a good LEED pattern is visible in all cases.

At this stage it is already apparent that a possible explanation of these observations in terms of an evolution of the surface state into an interface state, i.e., the persistence of the (Au 5$d_{xy}$)-like state at the Cr/Au interface as an interface state seems inappropriate since in that case it is very difficult to see why the state's intensity depends in such a drastic way on the substrate temperature during deposition. In this respect, it is noteworthy that

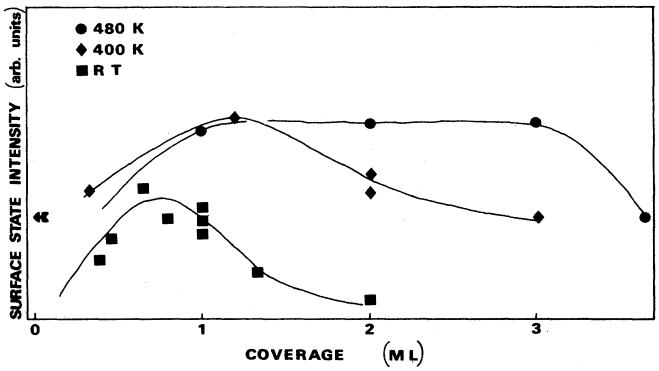

FIG. 2. Intensity of the Au(100)-(1$\times$1) $\overline{M}_3$ surface state vs Cr coverage of the Au(100) substrate held at various temperatures during deposition. The arrow indicates the intensity for the metastable Au(100)-(1$\times$1) surface prepared by mild ion bombardment.

LEED indicates a well-ordered overlayer at all temperatures. Thus, if simple layer-by-layer growth would occur along with the persistence of the Au surface state as an interface state, one would expect to observe for a given coverage essentially the same state's intensity irrespective of the deposition temperature and for a given deposition temperature an exponential decrease in intensity versus coverage in contradiction with the data of Fig. 2.

Figure 1 also indicates a shift to greater BE of the surface-state feature as the amount of Cr deposited on the surface increases. As summarized in Fig. 3, the state's location changes in a roughly linear way with Cr coverage from 1.8 eV at low coverages to 2.7 eV at 3–4 ML when Cr is deposited on the substrate above 400 K. Furthermore, for a given Cr coverage one observes generally a larger BE shift when deposition is carried out with the substrate at RT relative to higher temperatures. Where a comparison is possible with the measurements of Ref. 7, namely for substrate temperatures of 400 K, a good qualitative agreement is observed. However, note that we do not observe any distinct change in the surface-state peak width when the substrate temperature is held at 480 K. Figure 1 indicates that the full width at half maximum is about 0.35 eV essentially independent of Cr coverage.

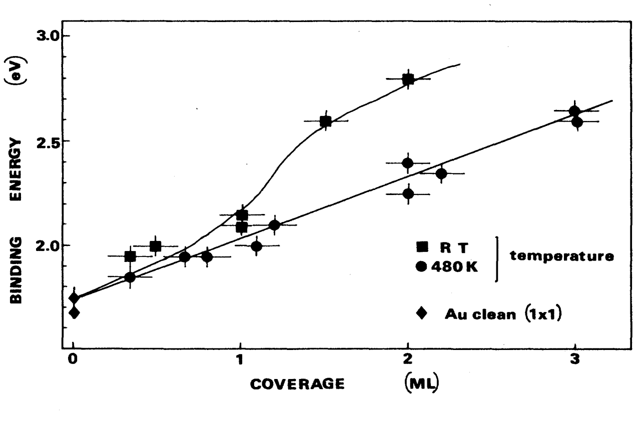

FIG. 3. Binding energy of the Au(100)-(1$\times$1) $\overline{M}_3$ surface state vs Cr coverage of the Au(100) substrate held at RT or at 480 K.

Again it is important to realize that the state's energy location ($\geq 2$ eV) for Cr coverages above 1 ML can hardly be explained within the view of epitaxial Cr growth in a layer-by-layer mode and evolution of the clean Au(100)-(1$\times$1) surface state into an interface state at the Cr/Au(100) interface. If this picture were indeed correct, the interface state would become degenerate with substrate bulk states of $X_5$ symmetry, derived from Au $5d_{xy,yz}$ states, responsible for the emission observed on top of the Au 5$d$ band near 2 eV BE. Yet, the Tamm surface state and, in turn, the interface state must be split off from those bulk states with compatible symmetry. Thus, strong hybridization and mixing would occur and the concomitant drastic damping of the interface state would most likely prevent its observation or at least result in a substantial broadening of the relevant spectral feature in contradiction with experiment. We demonstrate in the next section that all the observations can be readily explained in terms of Au-Cr alloying at the Cr/Au(100) interface.

## IV. FORMATION OF AN EPITAXIAL $Au_{1-x}Cr_x$ ALLOY WITH A GOLD-RICH SURFACE

Figure 4 displays photoemission spectra from epitaxial $Au_{1-x}Cr_x$(100) on Au(100) for $x = 0.15$, 0.30, and 0.45, respectively. Since the alloy overlayer thickness ($\sim$20 Å) is large with respect to the mean free path of the photoelectrons ($\sim$5 Å) the contribution from the Au substrate must be negligible. Thus the spectral features reflect the bulk and surface electronic structure of the alloy rather than any substrate or substrate-alloy interface properties. Also shown in Fig. 4 are the relevant spectra for 1, 2, and 3 ML of Cr deposited on Au(100) held at room temperature. Both series of spectra are taken at normal emission. The striking one-to-one correspondence between the spectra of both series indicates that a Au-Cr alloy must be formed at the Cr/Au(100) interface. The persistence of a good (1$\times$1) LEED pattern when Cr is deposited on Au(100) is then explained by the formation of an epitaxial $Au_{1-x}Cr_x$ superficial alloy. The concentration $x$ increases progressively up to 0.5 in the 0–3-ML range when Cr is deposited on Au(100) held at RT. At higher substrate temperatures and for a given Cr deposit, enhanced Cr diffusion into the substrate results in a lower Cr concentration in the superficial alloy. As shown in detail elsewhere,[4,8] a large body of experimental data can be readily explained in this way. In particular, it appears that the electronic structure of the alloy is well described by a split-band model[13,14] which is an extension to large concentrations of Friedel's virtual bound-state picture appropriate in the dilute alloy limit (small $x$). The feature visible near 1 eV BE in the spectra of Figs. 1 and 4 corresponds to electrons mainly localized on Cr sites. On the other hand, the states having greater probability density

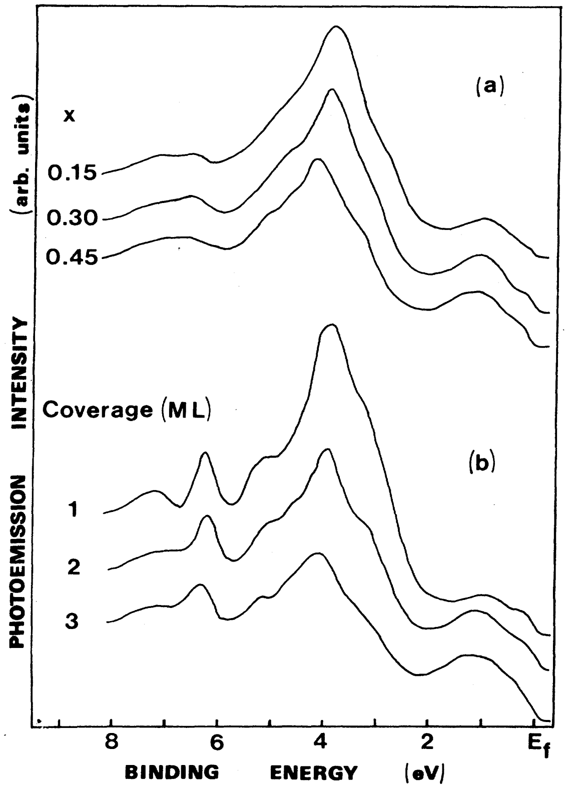

FIG. 4. Normal emission spectra taken with $\hbar\omega=21.2$ eV: (a) 20 Å of coevaporated epitaxial $Au_{1-x}Cr_x$ alloy films on Au(100), (b) Cr deposited on Au(100) kept at RT.

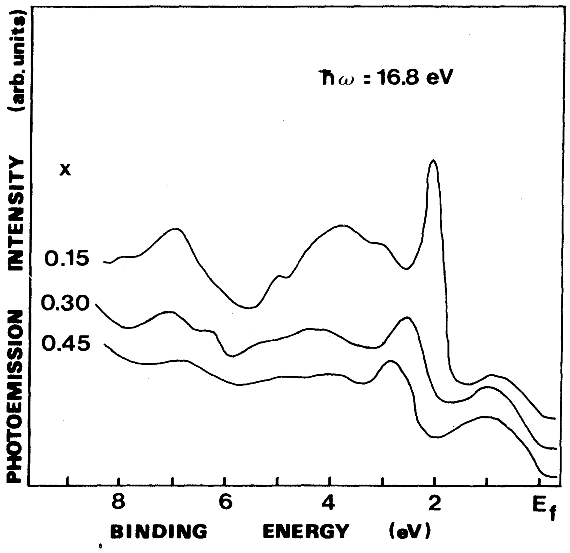

FIG. 5. Off-normal emission spectra probing the $\overline{M}$ point of the surface Brillouin zone for 20 Å coevaporated epitaxial $Au_{1-x}Cr_x$ alloy films on Au(100) and $x=0.15$, 0.30, and 0.45.

on Au sites reflect in the large structure in the 2–8 eV BE range. Of particular relevance here is the distinct narrowing of the Au 5*d* band with increasing Cr concentration visible in Fig. 4. The main effect of this narrowing which can be qualitatively explained in a simple tight-binding model is a shift to higher BE of the upper Au 5*d*-band edge.

Figure 5 presents spectra relevant to the same epitaxial $Au_{1-x}Cr_x$ overlayers as Fig. 4 but for a collection geometry probing approximately the $\overline{M}$ point of the $Au_{1-x}Cr_x(100)$-$(1\times1)$ [or Au(100)-$(1\times1)$] surface Brillouin zone. A comparison with the spectra of Fig. 1 reveals that the conspicuous narrow feature at 2, 2.5, and 2.8 eV for $x=0.15$, 0.30, and 0.45, respectively, is quite similar to the peak discussed in Sec. III as far as the width and energy location are concerned. Since the first Cr monolayers deposited on Au(100) form a Au-Cr alloy, both peaks must have the same origin. The continuous evolution of the relevant electronic state towards the clean Au(100)-$(1\times1)$ $\overline{M}_3$ surface state as $x$ in $Au_{1-x}Cr_x$ or the Cr coverage on Au(100) is reduced, along with the fact that in the case of thick $Au_{1-x}Cr_x$ alloy overlayers this peak cannot result from interface state emission leads us to an explanation in terms of a $Au_{1-x}Cr_x(100)$-$(1\times1)$ $\overline{M}_3$ surface state. In fact, there must be a strong tendency for Au segregation at the alloy surface since at low coverages ($<3$ ML) the Cr/Au(100) interface is surprisingly much less reactive than expected against oxygen adsorption. This can be seen in Fig. 6 where the Cr $2p_{3/2}$ line is shown before and after exposure to 3 L of oxygen for either 1 ML deposited at RT or 2 ML deposited at 480 K. In the RT case only about half the Cr is oxidized

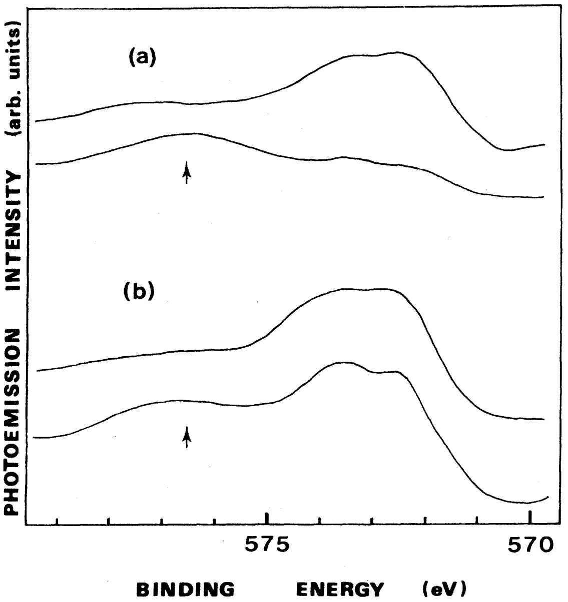

FIG. 6. Cr $2p_{3/2}$ core-line photoemission spectra before (upper curve) and after (lower curve) exposure to oxygen at saturation ($\sim3$ L): (a) 1 ML of Cr on Au(100) held at room temperature, (b) 2 ML of Cr on Au(100) held at 480 K. The structure in the clean spectra is due to multiplet splitting (see Ref. 8). The arrow indicates the energy location of oxidized species.

in these conditions while for deposition at 480 K essentially no oxidation is observed. This indicates that the alloy surface formed at 480 K is composed of a pure Au(100)-$(1\times1)$ layer, while at RT only part of the surface is made of Au(100)-$(1\times1)$ patches, the Au segregation process being diffusion limited.

We are now in a position where the observations of Sec. III can be simply explained. The Au $5d_{xy}$ orbitals of the Au(100)-$(1\times1)$ islands on top of the $\mathrm{Au}_{1-x}\mathrm{Cr}_x$ alloy still form a true $\bar{M}_3$ surface state for $0<x<0.5$. Indeed, because of the Au $5d$-band narrowing in the alloy the surface state is still located above the upper Au $5d$-band edge at all $x$. This prevents any hybridization with bulk $d$ states and thus explains the persistence of the state. More specifically, the shift in the state's binding energy closely follows that of the upper $d$-band edge. This is not surprising since a Tamm-like state, by its very nature, must be located in close proximity of the band edge from which it is split off. In a simple tight-binding model the energy splitting is related to the difference in surface and bulk potentials[15] which appears to be comparable for $\mathrm{Au}_{1-x}\mathrm{Cr}_x$ and pure Au. The localization of the state in the Au(100)-$(1\times1)$ top layer should be enhanced on $\mathrm{Au}_{1-x}\mathrm{Cr}_x$ since the coupling to Au $5d$ bulk states is reduced by the presence of Cr species.

It is now clear that all the substrate temperature effects described in Sec. III are merely the consequence of enhanced Cr diffusion into the Au lattice and segregation of Au at the alloy surface at higher temperatures. For instance, the larger shift of the surface-state energy observed for a given Cr deposit at RT relative to 400 or 480 K, shown in Fig. 3, is due to the limited Cr diffusion at RT since this results in a higher Cr concentration and, in turn, a narrower Au $d$ band in the superficial alloy. On the other hand, the surface-state peak exhibits its highest intensity for deposition at 480 K where a pure (100)-$(1\times1)$ top layer is formed as opposed to deposition at RT where Au segregation is strongly diffusion limited and therefore the state's intensity is reduced (by a factor of $\sim2$ at 1 ML Cr and much more at high coverages). Note that the smaller intensity observed on the metastable clean Au(100)-$(1\times1)$ surface is likely due to some disorder brought about by the ion-bombardment preparation method.

From all this evidence we conclude that Au(100)-$(1\times1)$ patches, present on top of the $\mathrm{Au}_{1-x}\mathrm{Cr}_x$ superficial alloy, are responsible for the persistence of the $\bar{M}_3$ surface state at the Cr/Au(100) interface. Clearly the extent of Au segregation at the alloy surface and, in turn, the surface state's intensity must be a strong function of temperature and Cr coverage in accord with experiment. In this respect, it is worthwhile to recall the observation first reported in Ref. 7 and confirmed in our experiments that deposition of 1 ML Au on a Cr/Au(100) interface prepared by deposition of 3 ML of Cr on clean Au(100) at room temperature (which exhibits no $\bar{M}_3$ state) results in the reappearance of the surface state. Obviously, the simplest explanation of this original behavior is that the deposited Au species form ordered Au(100)-$(1\times1)$ islands on top of an interfacial alloy, i.e., a situation similar to the one obtained by Au segregation at higher temperatures.

## V. CONCLUSION

The remarkable persistence of the Au (100)-$(1\times1)$ $\bar{M}_3$ surface state at the Cr/Au(100) interface up to several Cr monolayers (4 ML at 480 K) is a unique feature of this metal-metal interface. The interpretation in terms of interfacial epitaxial alloy formation with a Au-rich surface reveals an unusual and original mechanism for the persistence of a surface state on a substrate metal $A$ when a metal $B$ is deposited. The mechanism actually rests on a negative solution energy of metal $B$ in metal $A$ and can be thought of, in the high-temperature limit, as a dissolution of the $B$ species into $A$ leaving the original surface of metal $A$ unchanged. In the case of Cr/Au(100) the process is severely diffusion limited near RT and a finite amount of Cr in the superficial region is needed anyway in order to stabilize the $(1\times1)$ surface atomic arrangement responsible for the $\bar{M}_3$ state emission.

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