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## Rapid Communications

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# Surface states of clean and metal-overlayer-covered Cr(001) films

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Electronic-structure calculations for a clean Cr(001) film and for Cr(001) films covered with Au, Pt, or Ir monolayers predict a surface band localized on the outer Cr layer near the Fermi level. The high density of surface states in the Au adsorption case may help explain the recent observation of 3 K superconductivity in Au-Cr-Au sandwiches. The stability of the surface band against overlayer adsorption indicates the necessity of refining the test usually used to identify spectroscopic peaks as surface states.

In this Rapid Communication we wish to report the results of self-consistent surface electronic-structure calculations that indicate the presence of a band of surface states at the Fermi level of Cr(001) which is stable against metal overlayer adsorption. The results are of interest both because of recent evidence that a sandwich Au-Cr-Au film exhibits superconductivity,[1] and because the systematics of the stability of the surface band bears on the validity of a test which is widely used to identify surface states in surface spectroscopic experiments.[2]

The clean Cr(001) surface is in itself of interest. Unlike Mo(001) (Ref. 3) and W(001) (Refs. 3 and 4) it apparently does not reconstruct.[5] Below the Néel temperature of bulk Cr it is thought to be ferromagnetic.[6] The Au(001)/Cr(001) adsorption system is interesting because of the exceptionally close match in surface translation vectors, which makes it possible to grow a Au(001) crystal (axes rotated 45° with respect to those of the Cr) with a lattice strain of only 0.02%. Recently, Au-Cr-Au sandwich films have been prepared, for which the Cr thickness is 1–2 nm (7–14 Cr layers using the bulk bcc Cr lattice constant). The sandwiches, whose characterization is being improved,[7] were found to be superconductors, with transition temperatures as high as 3 K.[1] The results of various experiments[8,9] and of an electronic-structure calculation[10] have been used to argue that the superconducting transition is the result of a change in the Cr layer structure from bcc to fcc. (001) layers of fcc Au and bcc Cr are simple square arrays of atoms with successive layers stacked so that the atoms in one layer are in the fourfold hollow sites of the layer immediately below. For the fcc structure, the interplanar spacing is $1/\sqrt{2}$ times the in-plane atom spacing, while for bcc this ratio is $\frac{1}{2}$. Thus, for the presence of a Au substrate to induce a commensurate epitaxial fcc phase of Cr, long-range Au-Cr interactions must be postulated which expand the Cr interplanar spacing by exactly $\sqrt{2}$ throughout the Cr film. X-ray diffraction experiments[8] appear to confirm the existence of an epitaxial fcc phase of Cr.[9] These x-ray results, however, which imply an increase in the volume of the Cr unit cell by $\sqrt{2}$, are contradicted by extended x-ray absorption fine structure measurements[8] which indicate that the Cr-Cr spacing in thin Cr films adsorbed on Au is essentially the same as in bulk bcc Cr.

The electronic-structure calculation was performed for an fcc Cr crystal with a lattice parameter of 3.7 Å (i.e., not that of the commensurate epitaxial film discussed above, which is 4.08 Å).[10] A lattice constant of 3.7 Å was reported for fcc Cr in quenched Cr-Ni mixtures.[11] This phase is also believed to exist at temperatures near the melting point in pure Cr.[12] However, later work disputes this claim.[13] Evidence for a 3.7 Å fcc Cr phase has been reported for Cr adsorption on Au.[9] However, this work refers to incommensurate rather than commensurate epitaxy, and is for the Au(111) surface, not for Au(001). The calculation predicts a high density of states (DOS) at the Fermi level, in contrast to what is found for bcc Cr. This increased density of states was proposed to be the source of the rather high superconducting transition temperatures which have been found for the Au-Cr-Au sandwiches,[8,10] the assumption being that the Fermi-level density of states would remain high in the fcc phase even if the lattice parameter were stretched to 4.08 Å.

The electronic-structure calculation performed to explore the consequences of the existence of an fcc Cr phase was for bulk fcc Cr, not for a film.[10] Since we believe that the volume increase associated with the proposed fcc phase is unphysically large, we have sought an alternate explanation for the high Fermi-level density of states, which the sandwich superconductivity measurements appear to require. To this end we have performed calculations for sandwich geometries, as well as for a clean Cr(001) film. To be specific, we have performed self-consistent surface linearized augmented-plane-wave (SLAPW) electronic-structure calculations[14] for the following clean and metal-overlayer-covered, paramagnetic Cr(001) slabs: clean five-layer Cr(001), a four-layer Cr(001) film with a (1×1) monolayer of Au(001) adsorbed on either side, and four-layer Cr(001) films with the Au atoms successively replaced by Pt, Ir, and Os atoms. These latter calculations were done to gain an understanding of the mechanism stabilizing the surface band. The Cr layer spacings were all held fixed at the bulk Cr value (1.44 Å). The metal overlayers were chosen to lie at a distance from the outer Cr layer such that the overlayer metal atom-Cr distance was the average of the bulk Cr and bulk overlayer-metal nearest-neighbor distances.

In Fig. 1, we show calculated differences in muffin-tin-integrated local densities of states (MTLDOS's) for the various films. In each case we have subtracted the MTLDOS for the innermost Cr of the film from that for the outermost Cr. The shortness of the screening length in transition metals means that the MTLDOS of the innermost muffin tin of a four- or five-layer Cr film is already a fairly good representation of the bulk Cr MTLDOS. Therefore, a peak in the difference curves indicates a Cr surface-state band.

Consider now the clean Cr five-layer film plot in Fig. 1. There is a prominent surface-state band in the neighborhood of the Fermi level. This band has been identified in earlier calculations[15] and in photoemission experiments.[16] Because this band gives rise to a high density of states at the Fermi level its existence is favorable to superconductivity (although we make no attempt here to estimate any transition temperatures). The recent superconductivity measurement[1] was not performed on a clean Cr film, however, but on a Au-Cr-Au sandwich.

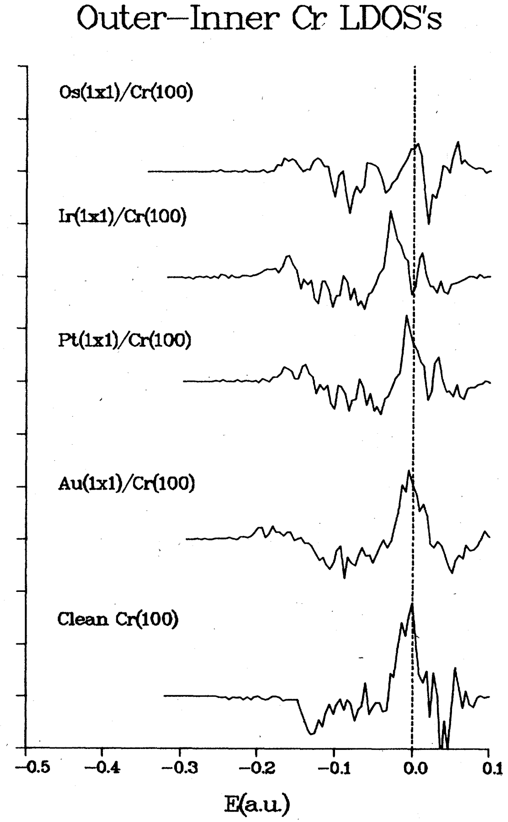

FIG. 1. Difference between the muffin-tin-integrated local densities of states between the outermost and innermost Cr layers, for the following film geometries: a clean, ideal, paramagnetic Cr(001) five-layer film, and four-layer Cr(001) films with (1 × 1) monolayers of Au, Pt, Ir, or Os adsorbed on both film surfaces.

A test that is often employed to identify those peaks in a photoemission experiment which represent surface bands is to cover the surface with a significant fraction of a monolayer of impurities.[2] One anticipates that the formation of bonds between the valence orbitals of the impurity atoms and the surface-state wave functions of the substrate will cause the surface band to disappear (possibly to reappear elsewhere in the spectrum). Our calculation, however, shows the contrary. As is seen in Fig. 1, the presence of a layer of Au on either side of a four-layer Cr(001) film has very little effect on the Cr surface band.[17] (Although, to be technically correct, it should now be renamed an interface band.) We found the same to be true in a calculation with two layers of Au on one side of the Cr film. We attribute this result to the fact that the *d* orbitals of Au lie too far below the Fermi energy to interact effectively with the *d*-like surface band of the Cr. Thus, one sees that the Fermi-level density of states in a Au-Cr-Au sandwich will be very much larger than in bulk Cr, comparable to what one would find for a clean Cr(001) film. Further calculations reveal that the same is true even if Au is replaced by Pt or Ir. For these metals, the Fermi level does intersect the *d* bands. However, it lies near the top of the *d* bands, where the wave functions are of antibonding character. On the other hand, in Cr, the Fermi level crosses the *d* bands in a region of bonding and nonbonding states, since Cr lies slightly to the left of the center of the 3*d* series. Thus, the symmetry of the Fermi-level states of Pt and Ir is different from that of Cr, which accounts for the fact that Pt and Ir overlayers do not remove the Cr(001) surface band. It is only when we move leftward in the 5*d* series to Os, that the overlayer causes the removal of the Cr surface band. This set of results has obvious implications for the generality of the impurity-adsorption test for surface states. Only those impurities whose valence orbitals are able to interact effectively with a surface-state band should be expected to cause its disappearance in an adsorption situation.

In summary, we have shown that one can account for a high Fermi-level density of states in a Au-Cr-Au sandwich without invoking an unusually large Cr volume change or structural change. One simply needs to look at a geometry which corresponds to that of the superconductivity experiment in which the high DOS was observed, namely, a Au-Cr-Au film. Of course the picture of superconductivity that emerges is somewhat different in our case from that which pertains to the fcc structure-change model. In the latter model, the high density of states exists throughout the volume-expanded Cr film. In our picture, there is only a high Fermi-level LDOS in the Cr surface monolayers. As a consequence one must imagine that below the critical temperature in a Au-Cr-Au sandwich one has two thin superconducting sheets, which short out three normal regions, i.e., the Au regions on either side of the Cr and the normal Cr region which separates the surface Cr monolayers.

The proximity effect would generally be thought to quench superconductivity in a film as thin as we are considering here (1 atomic layer) surrounded by two normal metals.[18] We can rationalize the survival of superconductivity by noting that the interface state electrons cannot communicate with the Fermi-level electrons in the normal metals. If they could, the interface state would not exist. We must assume that the effective barrier is adequate to reduce the penetration of the normal-state quasiparticles to the required degree.

Earlier experiments observing superconductivity with $T_c$ as high as 1.5 K in sputter-deposited Cr films may also be explained by the surface-state mechanism.[19] These films were shown by x-ray diffraction to be bcc with a lattice constant expanded by 1%–3% from the usual bulk value. This rules out an "fcc phase" explanation. However, the grain size in the films was small (120 Å) and a significant amount of the sputtering gas was trapped in the film, presumably on grain boundaries. Such internal surfaces could give rise to surface states related to those considered here. Our calculations show that the Cr(001) surface state which gives rise to the high Fermi-level density of states is stable against adsorption of monolayers of metals from the right-hand side of the $5d$ transition series. Thus, if the usual method of identifying surface states were used, adsorbing any of these metals on Cr one might be led to the false conclusion that the peak in the Cr DOS at the Fermi level is due to something other than the presence of a surface state.

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