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SP↔D CHARGE TRANSFER AT TRANSITION- AND NOBLE-METAL SURFACES: A REPLY

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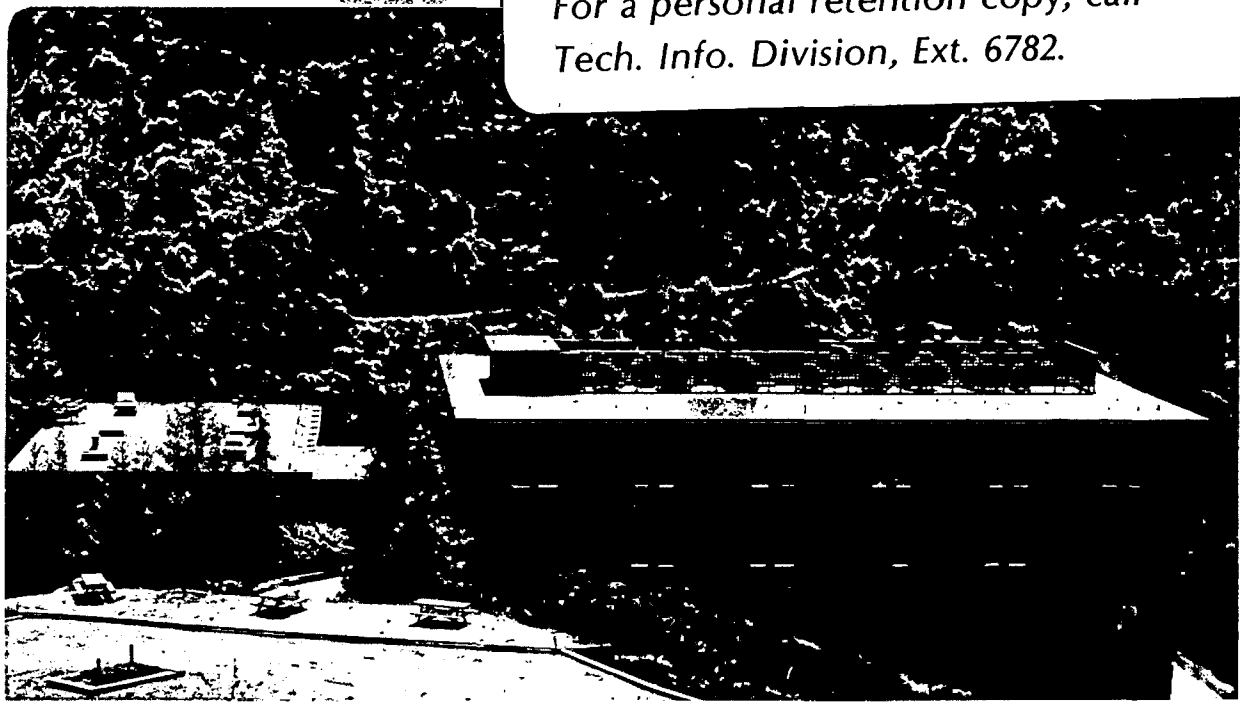

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sp↔d charge transfer at transition- and noble-metal surfaces: a reply

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Published results of fully self-consistent calculations refute the conclusions of the preceding Comment, which are based on a faulty analogy between Ni and Cu. The behavior of the d-band at the surface of transition metals is dominated by physical effects very different from those encountered in noble metals.

We believe the criticisms made of our work[1] in the preceding Comment are based on faulty reasoning, and the conclusions drawn above for Ni are unfounded. Self-consistent calculations for nickel[2,3] show a transfer of electrons into the d orbitals at the surface; this effect is also seen in iron[3]. These results directly contradict Kleinman's qualitative analysis and support our conclusions in Ref. 1.

The crucial point here is that for Ni, but not for Cu, the d band plays a dynamic role at the surface. The Comment above relies on an incorrect analogy between transition and noble metals. For noble metals such as Cu, the d band is essentially full and inert, and Kleinman's analysis is valid (and is in fact consistent with our own statements in ref. 1 regarding the treatment of Cu there). However for Ni, the analysis given above is simplistic, in that it does not take account of the crucial intersite interactions which play a large role in determining the surface d-band behavior. Only the effect of the on-site potential is considered. However effects such as d-d bonding and band narrowing depend mainly on the local geometry rather than on the on-site potential. Moreover, the polarization due to local asymmetry plays a crucial role at the surface; the extra d occupancy comes from electron transfer from the surface p orbitals[2]. (The same effect exists in Cu, but only causes electron transfer between the p and s states). An analysis which virtually

neglects all these effects as driving forces for the d-band behavior could only be justified a posteriori by comparison with results of a detailed calculation. As it is, the only fully self-consistent calculations we know of which are relevant here, are in quantitative agreement regarding the surface-induced filling of the local d band, despite the very different techniques used. (The work of Gallagher and Haydock[4], which includes no p orbitals, cannot be considered relevant for these purposes.)

In Ref. 1 we pointed out that our calculation certainly exaggerated the transfer of electrons from the sp band into the d band at the surface; a reliable quantitative estimate of the sp-d transfer at the surface would be of great interest. It is our hope that, in view of the possible significance for surface chemistry, the appropriate analysis of a fully self-consistent calculation could be made available in the future[5].

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2. C.S. Wang and A.J. Freeman, Phys. Rev. B 19, 793 (1979).

3. J. Noffke and L. Fritsche, J. Phys. C 14, 89 (1981). This work treats the bulk and the unsupported monolayer film. Kleinman's arguments for the surface apply equally to the monolayer film. Moreover, Wang and Freeman (Ref. 2 here) treat both monolayer and thicker films; they find d-band filling for the monolayer film which is about twice the magnitude of the surface d filling, and is in quantitative agreement with the monolayer d filling found here.

4. J.M. Gallagher and R. Haydock, Phil. Mag. B 38, 155 (1978).

5. F.J. Arlinghaus, J.G. Gay and J.R. Smith have reported precisely the sort of calculation called for here -- Phys. Rev. B 21, 2055 (1980). They do not however report any orbital occupancy analysis.

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