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Observation of a Tamm-Type state on Cu0.9Al0.1(100) surface: Disorder effects and bulk electronic structure of an alloy

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appear to come from commensurability. Rather it seems to be related to the particular hydrogen-bonding network which is present in the three compounds. Speculatively, one may rationalize their low λ as coming from a high ω_0 in the expression for λ, since high-frequency hydrogen motion may well couple to the electrons along the chains. As there is relatively little hydrogen bonding transverse to the chains, this explains the low η in GCP(Br), K(def)TCP, and Rb(def)TCP.

In conclusion, the new quasi one-dimensional conductor CsCP(N_3) exhibits both structural and physical properties which may be understood in the context of previously described partially oxidized tetracyanoplatinates. It also demonstrates that commensurability does not in itself give rise to unusual features in connection with the Peierls transition.

[1]For a recent review, see, for instance, J. M. Williams, A. J. Schultz, A. E. Underhill, and K. Carneiro, in "Extended Linear Chain Compounds," edited by J. S. Miller (Plenum, New York, to be published), Vol. 1, pp. 73–118.

[2]A. E. Underhill, D. J. Wood, and K. Carneiro, Synth. Met. 1, 395–405 (1980).

[3]J. M. Williams, in Molecular Metals, edited by W. Hatfield (Plenum, New York, 1979), pp. 337–368.

[4]R. K. Brown, D. A. Vidusek, and J. M. Williams, Inorg. Chem. 18, 801 (1979).

[5]A. Braude, A. Lindegaard-Andersen, K. Carneiro, and A. S. Petersen, Solid State Commun. 33, 365 (1980).

[6]A. E. Underhill and D. J. Wood, Ref. 3, pp. 377–383.

[7]S. Drosdziok and M. Engbrodt, Phys. Status Solidi (b) 72, 739 (1975).

[8]K. Carneiro, A. S. Petersen, A. E. Underhill, D. J. Wood, D. M. Watkins, and G. A. Mackenzie, Phys. Rev. B 19, 6279 (1979).

[9]D. J. Wood, A. E. Underhill, A. J. Schultz, and J. M. Williams, Solid State Commun. 30, 501 (1979).

[10]J. B. Nielsen and K. Carneiro, Solid State Commun. 33, 1097–1099 (1980). The results derived in this paper are approximate, but numerical calculations show that they are accurate to a few percent, when applied to the compounds considered here.

[11]B. Horowitz, H. Gutfreund, and M. Weger, Phys. Rev. B 12, 3174 (1975).

[12]L. Pauling, The Nature of the Chemical Bond (Cornell Univ. Press, Ithaca, 1940).

Observation of a Tamm-Type State on $Cu_{0.9}Al_{0.1}$ (100) Surface: Disorder Effects and Bulk Electronic Structure of an Alloy

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The electronic structure of a $CU_{0.9}Al_{0.1}$(100) single crystal has been studied with use of an angle-resolved photoemission technique. An intrinsic Tamm-type surface state is found to exist in the disordered alloy. The linewidth of the surface state is analyzed to deduce the disorder-induced smearing of energy levels. These and other experimental results are discussed in terms of the computed band structure of the alloy on the basis of coherent-potential approximation applied to a realistic muffin-tin Hamiltonian.

Angle-resolved photoemission spectroscopy (ARPES)[1] has proved in recent years to be an important experimental tool in clarifying the nature of bulk and surface electronic structure of perfect crystals. The application of this technique to disordered alloys has been hampered, in part, by metallurgical difficulties associated with preparing oriented single crystals of alloys with clean surfaces. For example, often during the anneal-sputter cleaning procedure, annealing

causes surface enrichment of one of the species, while subsequent sputtering yields an amorphous state. Furthermore, it is only during the last few years that the theoretical understanding of disordered alloys has reached the point where reliable predictions of their bulk electronic structure are possible within the framework of average-t-matrix and coherent-potential approximations as applied to a realistic muffin-tin Hamiltonian for the alloy[2]; the corresponding study of the alloy surface is largely nonexistent at this time.

In attempting to develop ARPES as a probe of alloys, we have studied surface and bulk states on several faces of a $Cu_{0.9}Al_{0.1}$ crystal using radiation.[3] This system was chosen because it permitted easy cleaning by Ar^+-ion bombardment and annealing. The elemental composition of the surface (monitored via low-energy Auger spectra of constituents) was within 10%–13% of bulk value, and the final surface yielded sharp (1×1) low-energy electron diffraction patterns, indicating that the surface was clean and perfect.

This Letter reports the first observation of a Tamm-type surface state[4] in an alloy. This state is found to be localized around the $\bar{M}$ symmetry point of the (100) two-dimensional surface Brillouin zone. We focus on the effects of disorder on the ARPES spectra. One important consequence of disorder is to broaden the energy levels and as a result increase the widths of spectral features in an alloy. (The peaks, even in a perfect crystal, possess finite widths because of various mechanisms by which excitations can decay.) Therefore, it should be possible, in principle, to determine the magnitude of disorder smearing by a line-shape analysis of the ARPES profile. We emphasize, however, that the structures associated with bulk transitions involve many initial states (often closely placed). This complicates the analysis of their shapes, and makes it difficult to isolate the disorder-smearing effects from the measurements.[5] In contrast, the ARPES peak corresponding to the surface state arises from a single component (i.e., the surface state). By comparing the width of the surface-state peak in Cu with CuAl, we are able to estimate the disorder smearing in a concentrated alloy for the first time.

Figure 1 summarizes our main experimental results. ARPES spectra of Cu(100) and CuAl(100) are seen to be quite similar. In fact, on the basis of measurements for various emission angles (not shown), we find that the peaks in the two
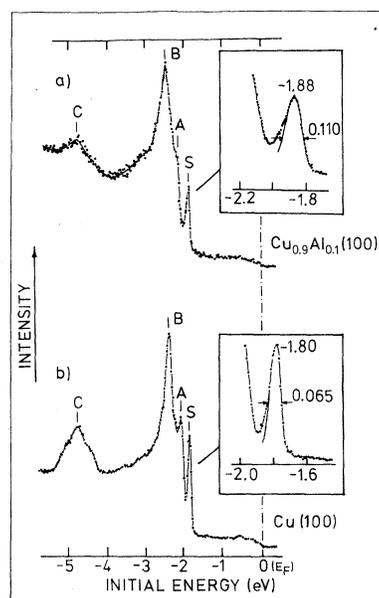

FIG. 1. Angle-resolved photoemission spectra obtained at the photon energy of 21.2 eV and the polar angle of emission of 63° for (a) $Cu_{0.9}Al_{0.1}$(100) and (b) Cu(100) single-crystal surfaces. Peaks labeled S are Tamm-type surface states. The insets show the peak S in detail.

spectra also possess a similar energy dispersion.[6] It is clear that the peaks in CuAl(100) can be associated with the same transitions as those in Cu(100). In particular, as in previous studies of Cu(100),[7–10] the peak S, which arises from a surface state located at $\bar{M}$ symmetry point in the surface Brillouin zone,[11] represents a Tamm-type state derived from the topmost (filled) d band along the W-X-W symmetry line in the Brillouin zone. Similarly, the peaks, A, B, and C in the alloy can be assigned to bulk transitions. In particular, the peak A (discussed below) arises from the topmost d band near the X-symmetry point in the Brillouin zone.

Bulk energy bands along the line $W \rightarrow X$ (which corresponds to the point $\bar{M}$ in the surface Brillouin zone) in Cu and $Cu_{0.9}Al_{0.1}$ are shown in Fig. 2, and will be used to interpret the present measurements. Note that the complex energy bands in the alloy (with imaginary parts representing disorder smearing) play a role essentially equivalent to that played by the more familiar Bloch energy bands in perfect crystals. Our computations are based on the use of realistic muffin-tin potentials for Cu and Al within the framework of the Korringa-Kohn-Rostoker scheme.[12,13] The coherent-potential approximation for random alloys was
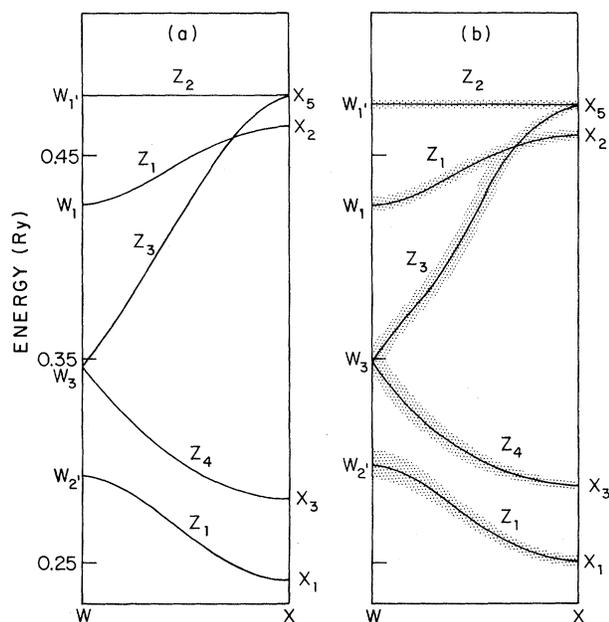
FIG. 2. Energy bands of d symmetry along the direction $W \to X$ in the Brillouin zone in (a) Cu and (b) $Cu_{0.9}Al_{0.1}$. The vertical length of shading around the bands in $Cu_{0.9}Al_{0.1}$ equals two times the imaginary part of energy. The Fermi energies for Cu and $Cu_{0.9}Al_{0.1}$ are 0.618 and 0.623 Ry, respectively.

employed to treat disorder effects in CuAl. The details of the calculations will not be described here, since these are discussed extensively in the literature.[2,12,14]

The bulk transitions in the alloy are considered first. Figure 2 shows that the complex bands in CuAl possess relatively small disorder smearing and remain well defined on the scale of their separations. Furthermore, the energy bands in Cu and CuAl are seen to be rather close in absolute energy. For these reasons, the similarity in the ARPES spectra in the two cases, noted previously in connection with Fig. 1, is to be anticipated. In fact, the calculations reproduce fine details of the measured level shifts. For example, peak A in CuAl shifts to a higher binding energy of 150 meV compared to Cu. (Note that the Fermi energies are lined up in Fig. 1.) This is in excellent accord with the corresponding computed value of 135 meV.[15] This level of agreement between experiment and theory is generally found for a number of other bulk transitions along ΓL, ΓKX, and ΓX.[16] While the details of such comparisons will be presented elsewhere, our primary conclusion concerning bulk transitions is that the states of d symmetry in Cu are not affected as much on the

addition of Al as those of s and p symmetry.

The question of the disorder smearing of the surface state peak S is taken up now. The observed full width at half maximum (FWHM) of peak S in Cu is 65 ± 5 meV and in $Cu_{0.9}Al_{0.1}$ it is 110 ± 10 meV. The main contributions to the linewidth arise from (i) lifetime of the photoexcited hole (excited-electron lifetime does not influence surface-state emission); (ii) finite energy and angular resolution of the analyzer; and (iii) the disorder broadening of the energy levels. The contribution due to the photoexcited hole is exceptionally small (≈ 40 meV),[8] because the hole created above the d band cannot decay via d-electron Auger transitions. To correct the linewidths for the energy resolution of the analyzer (the angular resolution has a negligible influence on the FWHM, because of the flatness of the Z_2 band), we proceeded as follows. The contour of peak S was regarded as a convolution of a Guassian, representative of the analyzer window function with the FWHM of 40 meV, and a Lorentzian function characteristic of the natural line shape of a hole state. From a simple approximation of the Voigt integral halfwidth, the corrected FWHM was found to be 40 meV in Cu (Ref. 8) and 95 meV in $Cu_{0.9}Al_{0.1}$. We attribute the remaining difference of 55 meV to the effect of disorder broadening.

We are not aware of any theoretical study of the disorder smearing of the Tamm state, with which the preceding results could be compared directly. The magnitude of the effect may, nevertheless, be estimated from bulk Korringa-Kohn-Rostoker–coherent-potential-approximation calculations. This is so because the Tamm state can be viewed as split off from, and thus composed of, states associated with the bulk Z_2 band,[4] which in the present case shows little energy dispersion and possesses an essentially $\vec{k}$-independent smearing [see Fig. 2 (b)]. Furthermore, the elemental composition of the surface is the same as the bulk. It is reasonable to argue, therefore, that the disorder broadening of the surface state should be close to that of the parent Z_2 band. In any event, the calculated value of 46 meV for the Z_2 band turns out to be in remarkable agreement with the value of 55 meV deduced above from measurements.

Finally, we note that the separations between the peaks S and A in Cu and CuAl are 180 and 280 meV, respectively (cf. Fig. 1). This increased separation can be understood qualitatively in terms of the constituent atomic potentials

used in the present computations. Because the Al muffin-tin potential is more attractive than that for Cu, the addition of Al causes an average lowering of the effective potential in the alloy. This would imply that the surface barrier in Cu becomes more repulsive on alloying, and hence should yield an increased separation between the Tamm-type surface and bulk states.[4,17]

In conclusion, we hope to have shown that ARPES experiments may provide a novel method of determining disorder broadening at least in the cases where a Tamm-type surface state exists in the alloy and the host. It is hoped that this work will stimulate further experimental and theoretical study of the problem.

[1]For a review, see N. V. Smith, in *Photoemission in Solids I*, edited by M. Cardona and L. Ley (Springer-Verlag, Berlin, 1978), p. 237.

[2]A. Bansil, Phys. Rev. Lett. 41, 1670 (1978); G. M. Stocks, W. M. Temmerman, and B. L. Gyorffy, Phys. Rev. Lett. 41, 339 (1978).

[3]The spectrometer used was a VG scientific ADES 400 equipped with XPS/AES/UPS/LEED techniques. The spectra were measured at the energy resolution of 40 meV and an angular resolution of 3°− 4° full opening of the electron beam cone.

[4]I. Tamm, Z. Phys. 76, 849 (1932); for a review, see F. Forstmann, in *Photoemission and the Electronic Properties of Surfaces*, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, New York, 1978), p. 193.

[5]In principle, earlier angle-resolved photoemission spectra of disordered alloys [M. Pessa, H. Asonen, M. Lindroos, A. J. Pindor, B. L. Gyorffy, and W. Temmerman, J. Phys. F 11, L33 (1981); H. Asonen and M. Pessa, Phys. Rev. Lett. 46, 1696 (1981)] have implied the existence of the band broadening but they have measured contours of groups of closely spaced spectral features rather than individual components.

[6]This would imply that the transitions involved in the alloy ARPES spectrum continue to be essentially $\vec{k}$ conserving.

[7]P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. Lett. 42, 1782 (1979); Phys. Rev. B 20, 3059 (1979). Recently, these authors have also investigated the existence of surface states in $Ni_{0.84}Cu_{0.16}$-alloy single crystals [Solid State Commun. 37, 519 (1981)]. However, as they point out, their results are essentially due to a surface monolayer of Cu.

[8]S. D. Kevan and D. A. Shirley, Phys. Rev. B 22, 542 (1980).

[9]D. Westphal and A. Goldman, Surf. Sci. 95, L249 (1980).

[10]J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. Lett. 42, 332 (1979).

[11]We emphasize that photoemission probes the same $\vec{k}$ region in Cu and $Cu_{0.9}Al_{0.1}$ because the lattice parameters are nearly equal for both the crystals.

[12]R. Prasad, S. C. Papadopoulos, and A. Bansil, Phys. Rev. B 23, 2607 (1981).

[13]Mattheiss's prescription was used to construct the muffin-tin potentials for constituents. Atomic configurations of $3d^{10}4s^1$ and $3s^2 3p^1$ for Cu and Al were employed. In both cases, the atomic Herman-Skillman charge densities were overlapped on an fcc lattice of lattice constant $a = 6.8309$ a.u. The Cu muffin-tin potential is identical to that used in Ref. 12, and yields Fermi surface and principal energy gaps in Cu in excellent agreement with relevant experiments. The effects of lattice expansion and of possible "charge transfer" between the constituents were incorporated as in Ref. 12. We avoid further details here because the results and conclusions of this article are insensitive to these uncertainties inherent in the first-principles band theory of metals and alloys.

[14]A. Bansil, Phys. Rev. B 20, 4025, 4035 (1979).

[15]The shift in the top of Cu d band on alloying is essentially $\vec{k}$ independent and may be monitored via the Z_2 band in Fig. 2. Note also that, of the total calculated shift of 135 meV, 62 meV is associated with the lowering of the d band, and the remaining 73 meV arises from the upward movement of the Fermi energy.

[16]The energy and $\vec{k}$ values for several individual levels in Cu and Cu Al were determined by the triangulation method [see, for example, M. Pessa, Solid State Commun. 39, 605 (1981)] without any auxiliary assumptions on the band structure. On this basis, level shifts for specific bulk states were deduced.

[17]On the basis of these potentials, we have carried out simple estimates of the increase in separation, employing perturbation theory. The calculated effect is of the same order of magnitude as the measured values.