# Self-consistent band structure of ordered β-brass*

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A comparison of self-consistent charge distributions and density of states for elemental bcc copper and zinc and ordered CuZn shows that in the compound, a net flow of electronic charge from zinc to copper occurs and a $3d$-band narrowing of a factor of 2 results from the decrease in overlap between like atoms.

## I. INTRODUCTION

The state of the art in band calculations has progressed to the point where self-consistent charge densities and band energies can be routinely generated. Closure of the self-consistency loop removes many of the obscuring uncertainties and permits detailed studies of Fermi surfaces[1] and photoemission of elemental solids. This paper represents the extension of the same physical model and computational techniques to the cesium chloride structure. The study of β-brass (CuZn) is motivated by the existence of (i) earlier non-self-consistent band calculations,[2-4] (ii) photoemission measurements which clearly display the location in energy of the Cu and Zn $d$ bands,[5] and (iii) optical measurements.[6]

In this paper, we report the results of four independent self-consistent band calculations. Two CuZn calculations were done in order to study the effects of small changes in the muffin-tin radii of the constituent atoms. Two additional calculations were made, one for bcc CuCu and one for bcc ZnZn with the same lattice spacing as CuZn in order to have a basis for comparison of the crystal charge distributions and the density of states. These two latter calculations allow us to study difference in charge distributions and in density of states between hypothetical elemental solids and the compound. We find that, in the compound, there is a net flow of electronic charge from the outer regions of the zinc atoms to the outer regions of the copper atoms and there is a considerable narrowing of the copper and zinc $3d$ bands.

This paper is organized as follows. In Sec. II, we review the computational techniques used in the calculations and identify the fundamental assumptions and approximations made. Section III gives our results for the band energies and compares these results with those of several other calculations. In Sec. IV, we present our density-of-states results showing band narrowing and we compare these with photoemission measurements. Finally, in Sec. V, we present evidence to show that considerable charge redistribution occurs in the compound and we present our over-all conclusions of considerable spillover of excess mobile charge from the outer portion of the zinc atom to the outer portion of the copper atom.

## II. CALCULATIONS

The band calculations use the Green's function method of Korringa, Kohn, and Rostoker[7] (KKR), which has been made fast enough[8] to permit self-consistent treatment of compound structures. Both potential and charge densities are assumed to have the "muffin-tin" form, i.e., spherically symmetric within the nonoverlapping spheres associated with each constituent and constant in the interstitial regions. This assumption, which is used extensively in band calculations, is known to be approximately valid for closely packed structures. The exchange and correlation contributions to the potential are obtained as in the $X\alpha$ method[9] but with the scaling parameter $\alpha$ determined by an empirical fit to the Fermi surface of elemental copper.[1] This value ($\alpha = 0.77$) is somewhat larger than the theoretical value ($\alpha = 0.71$) found by Schwartz[10] for atomic copper by fitting Hartree-Fock total energies. Although we have no empirical value for zinc, theoretical estimates of the atomic-number dependence of $\alpha$ suggests similar values for copper and zinc. We therefore used the empirical value $\alpha = 0.77$ throughout. The starting point of the calculation is a superposition of Herman-Skillman[11] copper and zinc atomic-charge densities. This charge density (or the crystal charge density during the iteration to self-consistency) is spherically averaged in each atomic muffin tin, and is replaced by a constant, chosen to make the unit cell neutral, in the interstitial region. The Coulomb potential due to this charge density can be regarded as the sum of the potentials of neutral, spherically symmetric, charge distributions in each muffin tin, and the potential due to nuclei of reduced charge embedded in a constant negative background. The former potentials are obtained by straightforward integration

of Poisson's equation in each muffin tin, and the muffin-tin average of the latter potential involves only two lattice sums, which can be related to similar sums for the simple cubic and body-centered-cubic lattices. Values for these have been given by Coldwell-Horsfall and Maradudin.[12] The exchange potential, which is a simple function of the charge density in the $X\alpha$ method, is added in and finally the interstitial average of the resulting potential is subtracted in order to make the final potential zero in the interstitial region.

The wave functions and band energies are found by the KKR method on a uniform $k$-space mesh corresponding to 203 points in the irreducible $\frac{1}{48}$th wedge of the Brillouin zone. A generalization of the method of Gilat and Raubenheimer[13] is used to determine the density of states and to locate the Fermi energy.

The new crystal charge density $\rho$ found by summation over occupied one-electron orbitals is then compared with the input charge density $\rho'$. For self-consistency, we require that

$$4\pi \int_0^{R_{MT}} r^2 dr \, | \, \rho'(\vec{r}) - \rho(\vec{r}) \, | < 0.005 \qquad (1)$$

for each muffin-tin sphere, where $R_{MT}$ is the appropriate muffin-tin radius. If the self-consistency criterion is not satisfied, a linear combination of $\rho$ and $\rho'$ is used to construct a new potential for the next iteration and a complete KKR band calculation is carried out with both core and valence states free to readjust. Self-consistency is usually achieved in about 30 iterations and yields band energies stable to within 0.01 eV.

Two complete self-consistent band calculations using the measured CuZn lattice parameter, $a = 5.5819$ a.u., were done. In one case the potential was constructed using muffin-tin spheres with equal radii (2.4170 a.u.), while in the second case, muffin-tin spheres of unequal radii (2.3771 a.u. for copper and 2.4569 a.u. for zinc) were used. The muffin-tin radii for the second calculation were determined by considering a superpo-
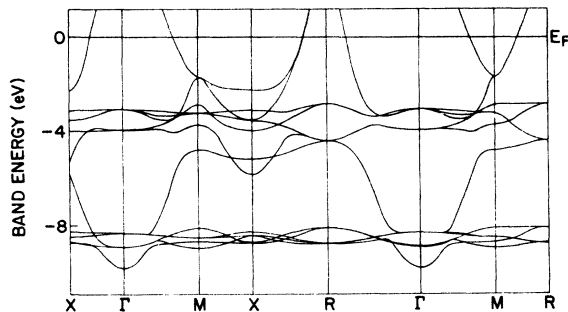
TABLE I.  Band energies relative to $E_F$ in eV.

| Band index | $X$ | $\Gamma$ | $M$ | $R$ |
|---|---|---|---|---|
| 12 | $-2.254$ | $>1.193$ | $-1.694$ | $>1.193$ |
| 11 | $-3.115$ | $-3.048$ | $-1.694$ | $>1.193$ |
| 10 | $-3.541$ | $-3.048$ | $-2.854$ | $-2.835$ |
| 9 | $-3.541$ | $-3.048$ | $-3.217$ | $-2.835$ |
| 8 | $-4.009$ | $-3.937$ | $-3.217$ | $-4.414$ |
| 7 | $-5.272$ | $-3.937$ | $-3.736$ | $-4.414$ |
| 6 | $-5.907$ | $-8.425$ | $-4.834$ | $-4.414$ |
| 5 | $-8.427$ | $-8.425$ | $-8.220$ | $-8.210$ |
| 4 | $-8.623$ | $-8.425$ | $-8.614$ | $-8.210$ |
| 3 | $-8.623$ | $-9.003$ | $-8.614$ | $-8.869$ |
| 2 | $-8.854$ | $-9.003$ | $-8.833$ | $-8.869$ |
| 1 | $-8.919$ | $-9.878$ | $-9.069$ | $-8.869$ |

sition of Herman-Skillman atomic potentials for copper and zinc and finding the radial position of zero derivative.

The two calculations yield almost idential energy bands with the copper $3d$ bands and the $s$ and $p$ bands agreeing to within 0.01 eV throughout the Brillouin zone. However, the unequal radii calculation gives a constant downward shift of about 0.07 eV for the zinc $3d$ bands. Although the differences are all small, we note that they are consistent with our experience in band calculations. The zinc $3d$ bands, which are very narrow and lie about 10 eV below the Fermi energy $E_F$, are very sensitive to computational details.

### III. COMPARISON

Since our two calculations yield almost identical results, we concentrate on the unequal-radii calculation. The energy bands along the symmetry directions of the Brillouin zone are shown in Fig. 1 and listed, for the symmetry points $X$, $\Gamma$, $M$, and $R$, in Table I in order of decreasing band index such that there is a direct correspondence between the band plot and the table. Coming up from low energies up, we see (i) a low-lying $s$ band near $\Gamma$, (ii) a zinc $3d$ band centered near $-9.5$ eV and approximately 1.0-eV wide (all energies are relative to the Fermi energy), (iii) a mixture of $s$- and $p$- plane-wave-like states, and (iv) a copper $3d$ band approximately 1.5-eV wide just below the Fermi energy. The copper and zinc $3d$-band widths, at the symmetry points of the Brillouin



FIG. 1.  Band energies for ordered $\beta$-brass.

TABLE II.  $3d$-band widths in eV.

| | $X$ | | $\Gamma$ | | $M$ | | $R$ | |
|---|---|---|---|---|---|---|---|---|
| | Cu | Zn | Cu | Zn | Cu | Zn | Cu | Zn |
| This work | 0.89 | 0.49 | 0.89 | 0.58 | 0.88 | 0.85 | 1.58 | 0.61 |
| Skriver and Christensen[a] | 0.85 | $\cdots$ | 0.89 | 0.42 | 0.90 | $\cdots$ | 1.54 | 0.53 |
| Arlinghaus[b] | 0.88 | 0.53 | 0.95 | 0.46 | 1.00 | 0.66 | 1.61 | 0.54 |

[a]Reference 4.          [b]Reference 2.

TABLE III.   Edge of copper $3d$ band relative to $E_F$ in eV.

|  | $X$ | $\Gamma$ | $M$ | $R$ |
|---|---|---|---|---|
| This work | $-3.12$ | $-3.05$ | $-3.22$ | $-2.84$ |
| Skriver and Christensen | $-3.12$ | $-3.09$ | $-3.32$ | $-2.89$ |

zone, are listed in Table II along with the corresponding widths as calculated by Arlinghous[2] and by Skriver and Christensen.[4] As Table II shows, we find slightly wider zinc $3d$ bands than Arlinghaus (except at $X$ where they are nearly equal) and copper $3d$-band widths which agree with Skriver and Christensen to within 0.04 eV.  In Table III we compare the top of our copper $3d$ bands with the Skriver-Christensen results and again see good agreement.

The most striking difference between our calculations and those of Arlinghaus and of Skriver and Christensen is the existence of an $s$ band at $\Gamma$ which extends well below the zinc $3d$ bands.  The source of these differences in detail must be either in the different treatment of exchange (they use full Slater exchange while we use an empirical exchange with $\alpha = 0.77$) or must be a consequence of self-consistency.

Except for small differences in detail, we find remarkable over-all agreement with the non-self-
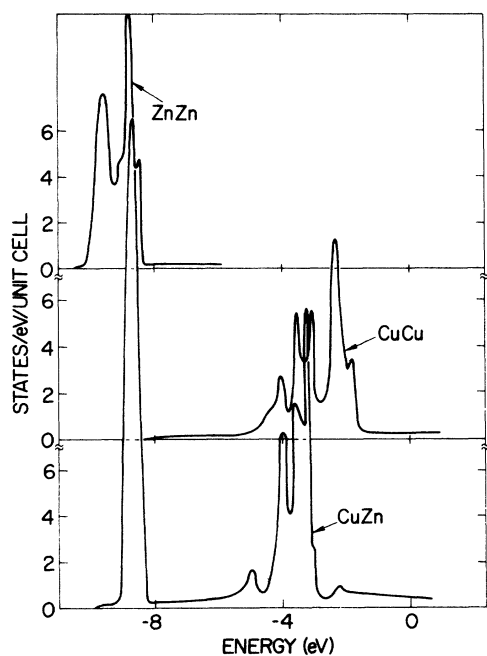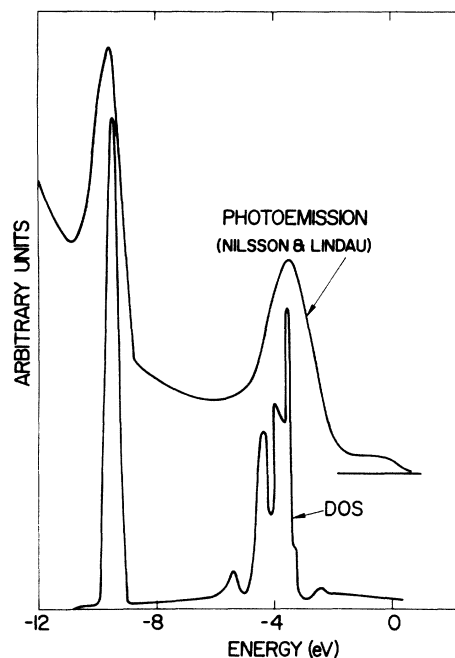


FIG. 3.   Density of states with $(m/m^*) - 1 = 0.08$ and high-energy photoemission.

consistent results of the comparison calculations. This supports the general lore that non-self-consistent band calculations using full Slater exchange can approximate the results of self-consistent calculations using more reasonable (either theoretical or empirical) exchange.

## IV.  DENSITY OF STATES AND PHOTOEMISSION

The density of states $N(E)$ for CuZn, CuCu, and ZnZn (i.e., bcc, Cu, and Zn with the same lattice



FIG. 2.   Density of states for CuZn, CuCu, and ZnZn, all with the same lattice.
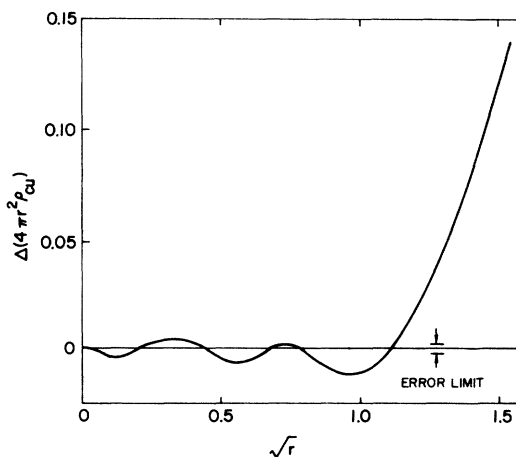


FIG. 4.   Difference in $4\pi r^2 \rho$ between a copper atom in CuZn and in CuCu.
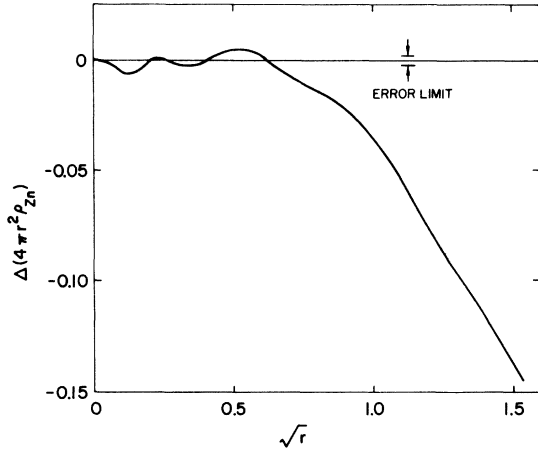
FIG. 5.  Difference in $4\pi r^2 \rho$ between a zinc atom in CuZn and in ZnZn.

as CuZn) are shown in Fig. 2 where in all cases, the energy values refer to the respective Fermi levels. At 20% of peak value, a band narrowing of approximately a factor of 2 is apparent in the compound for both the copper $3d$ bands and the zinc $3d$ bands. In addition, we see the appearance of two distinct peaks, one on each side of the main copper peak in CuZn which we identify, by comparing with the band plot of Fig. 1, as being due to band mixing or hybridization near the Brillouin-zone face defined by symmetry points $M$, $Z$, and $R$.

The results represented in Figs. 1 and 2 are ground-state results only and should not be compared directly with experiment. For excited state properties, it has been shown[14] that an energy-dependent correction which alters all eigenvalues according to

$$\Delta E_i = (E_i - E_F)(m/m^* - 1) \qquad (2)$$

can be used. This has the effect of spreading all bands relative to $E_F$ by an amount proportional to $(m/m^*)$ − 1, the electron-electron effective mass correction. In the density-of-states curves, the correction amounts to spreading the curves holding $E_F$ constant. Our experience with elemental copper indicates that a value of $(m/m^*)$ − 1 = 0.08 gives a reasonable fit to both $\epsilon_2$ and photoemission data. Figure 3 displays the result of applying the same correction to the density-of-states curve of CuZn along with the photoemission results of Nilsson and Lindau.[5] The

theory indicates Cu $d$ bands ~2 eV wide and ~4 eV below $E_F$, and Zn $d$ bands ~1 eV and ~9.5 eV below $E_F$. The greatest deviation from experiment lies in the width of both sets of $d$-bands. We suspect that the photoemission data contain broadening, perhaps due to disorder in the crystal, not accounted for in our density of states. Our suspicion of experimental broadening is based in part on the complete absence of internal structure in the measured $d$ bands. In particular, we note that there is no experimental indication of our "zone-face" bands whose existence should be insensitive to the details of the theory.

## V.  CHARGE REDISTRIBUTIONS

The electronic charge distribution associated with a given atom in a solid depends upon the atomic environment. In Fig. 4, we describe the difference between copper in CuZn and copper in bcc CuCu by plotting

$$\Delta(4\pi r^2 \rho)_{Cu} \equiv (4\pi r^2 \rho_{Cu})_{CuZn} - (4\pi r^2 \rho_{Cu})_{CuCu} \qquad (3)$$

vs $r^{1/2}$. Figure 5 is the corresponding curve for zinc. From these curves, we see that in CuZn, there is a net buildup of charge around the copper atoms and a net depletion of charge around the zinc atom relative to the bcc elemental structures with the same lattice constant. We take this as evidence of charge transfer from zinc to copper in forming the compound. We make no attempt to calculate the total charge transfer because this would require a precise definition of the spacial boundaries associated with each atom.

Figures 4 and 5 show that the charge redistribution is concentrated in the outer regions of the atoms. Since the core regions $(r^{1/2} \lesssim 1.0)$ show only slight changes, we conclude that the core charges do not contribute to the charge transfer. That is, the total core charge does not change appreciably.

The error limits shown are based on our self-consistency requirement as expressed in Eq. (1), assuming a constant error throughout the spatial extent of the charge distribution. The apparent core oscillations are therefore seen to be somewhat greater than the errors in our calculations.

## ACKNOWLEDGMENTS

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