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Electronic Structure of Alpha Brass*

H. AMAR, K. H. JOHNSON,† AND C. B. SOMMERS
Temple University, Philadelphia, Pennsylvania

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We have investigated the band structure of alpha brass (α-CuZn) as a function of its composition, over a range of 5 to 30% Zn, by steps of 5%. The Kohn-Rostoker method was used in combination with a spherical-average model potential. The conduction bands were determined at high symmetry points of the Brillouin zone. It was assumed that the Cu *d* bands are unchanged by alloying. It was found that the conduction bands are displaced to lower energies, the $L_{2'}-L_1$ gap across the {111} faces of the zone is reduced by 1.3 eV at 30% Zn, and the Fermi surface approaches the {200} faces of the zone. Our results are used to interpret the measured optical properties (Rayne and Biondi, Green), and to give a semiquantitative discussion of the theory of alloying and alpha-phase stability.

I. INTRODUCTION

In two earlier papers[1,2] (heretofore denoted I and II) we have described the electronic structures and Fermi surfaces of *ordered* and *disordered* beta-phase binary alloys of the IB-IIB columns of the periodic table. In this work we present the results of our investigation of the band structure of α-CuZn as a function of composition. Several models and theories, old and new (Mott and Jones,[3] Jones,[4–6] Konobejewski,[7] Cohen and Heine,[8] Friedel,[9] Hume-Rothery,[10] Hume-Rothery and Roaf,[11] and Lettington[12]) have been proposed to explain the stability and the various electronic properties of the alpha-phase alloys. Our calculations provide perhaps the first semiquantitative test of these models.

We have used the Kohn-Rostoker (KR)[13] method in combination with a "pseudo-periodic" potential.[14–16] The details of this method as well as its advantages and limitations are discussed in (I) and (II). It is sufficient here to say that the approximation reduces to a choice of an average model pseudo-potential around any lattice site which takes the form

$$\bar{V}(r)=(1-C)V_A(r)+CV_B(r). \qquad (1)$$

$V_A(r)$ and $V_B(r)$ are the appropriate "muffin-tin" potentials for the individual solvent and solute atoms, respectively, and C is the solute concentration.

We also apply this technique to determine the conduction bands of α-CuZn as a function of solute concentration. The "pseudo-periodic" model breaks down in the case of localized or semilocalized ion-core states [refer to IIIA of (II)]. Therefore we have assumed that the Cu *d* bands in the alloy are unchanged on the energy scale from those found in the pure metal. The possible effects of alloying on these bands are considered in the final analysis. As in (II), the Cu and Zn potentials of Herman and Skillman[17] (H-S) have been used to construct the conduction-state potentials. The bands have been computed for the symmetry points Γ, X, and L of the zone. The concentration C has been varied at steps

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† Present address: Quantum Theory Group, University of Florida, Gainesville, Florida.

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[16] J. L. Beeby, Phys. Rev. **135**, A130 (1964).

[17] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

of 5% and over a total range of 0–30% Zn concentration. The bands have been adjusted so that for 0% Zn they agree exactly with those obtained by Segall[18] for pure Cu (using an l-dependent potential).

II. BAND PROFILES

The energy eigenvalues $E(k)$ are listed as a function of composition in Table I. The variations are smooth, but not entirely uniform, through the 30% range of Zn concentration. The error involved in the graphical interpolation of the KR secular determinants to zero amounts to ±0.01 Ry. The band profiles of Cu (solid curves) and α-$Cu_{0.70}Zn_{0.30}$ (dotted curves) are plotted in Fig. 1 along the $\langle 100\rangle$ $(\Gamma\Delta X)$ and $\langle 111\rangle$ $(\Gamma\Lambda L)$ direction of the zone.

TABLE I. Conduction-band energies (in Ry) for α-CuZn over a 0–30% range of Zn concentrations. Results for 0% Zn are those of Segall.[a] Interpolation error is ±0.01 Ry.

	0%	5%	10%	15%	20%	25%	30% Zn
Γ_1	−0.836	−0.85	−0.87	−0.88	−0.88	−0.89	−0.89
$X_{4'}$	−0.029	−0.04	−0.05	−0.05	−0.06	−0.07	−0.08
X_1	+0.389	+0.38	+0.37	+0.36	+0.35	+0.34	+0.33
$L_{2'}$	−0.247	−0.25	−0.26	−0.27	−0.28	−0.28	−0.29
L_1	+0.189	+0.16	+0.12	+0.11	+0.10	+0.08	+0.05

[a] See Ref. 18.

The predominant effect of alloying is a general displacement of the conduction bands to lower energies. The shifts of the Γ_1, $X_{4'}{}'$, X_1, and $L_{2'}$ levels are of the same order of magnitude. The decrease in L_1 is somewhat larger, resulting in a reduced $L_{2'}$-L_1 energy gap. Another effect of alloying is the appearance of a narrow Zn d band (not shown in Fig. 1) approximately 0.2 Ry below the Γ_1 level.

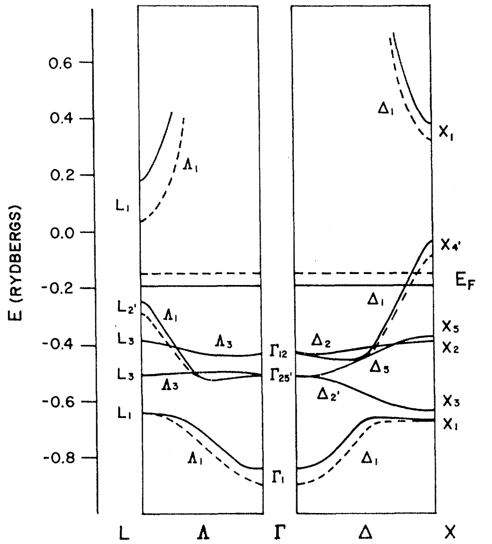

FIG. 1. Comparison of energy bands of α $Cu_{0.70}Zn_{0.30}$ (dotted curves) with those of Cu (solid curves).

The rather "rigid" displacement of the conduction bands downward is not unusual in view of our starting assumptions. By choosing an average potential based on the use of the neutral free-atom potentials $V_A(r)$ and $V_B(r)$, we have tacitly assumed that the excess 4s electron of Zn spends most of its time in the vicinity of the Zn^+ ion. This is consistent with Friedel's[9] proposal that the excess charge on the nucleus of the solute atom is locally screened out by the excess electronic charge. Moreover, Friedel[9] has shown that such a model is perfectly consistent with the "rigid-band" theory that alloying shifts the energy of every state by a constant amount.

The shift of the Fermi level from the value calculated by Segall[18] for Cu has been measured with respect to the reduced Γ_1 level (see dotted line in Fig. 1). It is reasonable to assume this shift is also given by the rigid-band approximation. It is important to note, however, that the increase of E_F with respect to the top of the d band is considerably less than it would be if the d band were treated in the same way as the conduction bands.

The reduction of the $L_{2'}$-L_1 energy gap is significant because of its bearing on the Fermi-surface topology. Cohen and Heine[8] have predicted a decrease in this gap together with a sphericization of the Fermi surface. Actually, the computed decrease of the $L_{2'}$ energy coupled with the increase in E_F imply a slight increase in overlap area of the Fermi surface with the {111} faces of the zone. The lowering of the $X_{4'}$ energy plus the increase in E_F indicate the approach of the Fermi surface to the {200} faces.

III. OPTICAL PROPERTIES

Biondi and Rayne[19] have measured the optical absorbtivity of alpha brass over a range of composition extending to 30% Zn. The absorption edge occurring at 2.2 eV in Cu shifts to approximately 2.6 eV in the case of α-$Cu_{0.70}Zn_{0.30}$. This edge has been attributed to direct electronic transitions[20] and/or indirect transitions[21] between the d band and the Fermi level near $L_{2'}$. The calculated increase of E_F with respect to the top of the d band in the present work is 0.48 eV, as compared with the optical result of 0.36 eV. The theoretical bands agree with those proposed semiempirically by Lettington[12] from the analysis of the optical data with respect to their shapes and shifts. However, the downward displacement of the $X_{4'}$ level is not as large as that predicted by Lettington.[12] This prediction was based on the observed reduction of 1.3 eV in the position of the secondary high-energy absorption peak which lies at

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[19] M. A. Biondi and J. A. Rayne, Phys. Rev. **115**, 1522 (1959).

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[21] C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1030 (1964); *ibid.* **136**, A1044 (1964).

4.2 eV in pure Cu. Transitions across the $L_{2'}$-L_1 gap have also been associated with this absorption.[20,21] The computed decrease of this gap is 1.3 eV, agreeing with the observed value.

IV. ALPHA-PHASE STABILITY AND THE DENSITY OF STATES

Let $N(E)dE$ denote the number of conduction electrons (in a binary alloy of given composition) with energies in the range E to $E+dE$. In the rigid-band approximation one assumes that upon changing the composition by increasing the number of solute atoms, the Fermi level is increased by a corresponding amount ΔE, the shape of the density of states curve, remaining unaltered. The total energy $\mathcal{E}(E)$ of all conduction electrons with energy less than or equal to E, is given by the area under the curve $EN(E)$ versus E. In his interpretation of the Hume-Rothery rules for alloys Jones linked the stability and the free energy of the alloy phase to minima of the function $\mathcal{E}(E)$. These minima can in general be determined by inspection of the density-of-states curve $N(E)$ versus E. Obviously the shape and size of the Brillouin zone play a decisive role.

This approach has often been mentioned and used by Jones and others using very general models. We are attempting here to apply the method using the actually calculated bands of α brass. In Fig. 2, we give approximate profiles of the density of states curves for pure Cu (solid line) and for $Cu_{0.70}Zn_{0.30}$ (dotted line), with corresponding Fermi levels.

It is suggested that the reader refer to Fig. 1 in order to better understand the shifts in the D.S. (density of states). Here one notices that for $Cu_{0.70}Zn_{0.30}$ the L_1, $L_{2'}$, X_1, $X_{4'}$, and Γ_1 level are shifted to lower energies (dotted line) with respect to the pure Cu levels (solid line). It should also be noticed that the largest contributions to the density of states at energies between -0.35 and 0.0 Ry come from the profiles centered near $L_{2'}$ and $X_{4'}$, respectively. It is for this reason that the peaks in Fig. 2 have been so labeled.

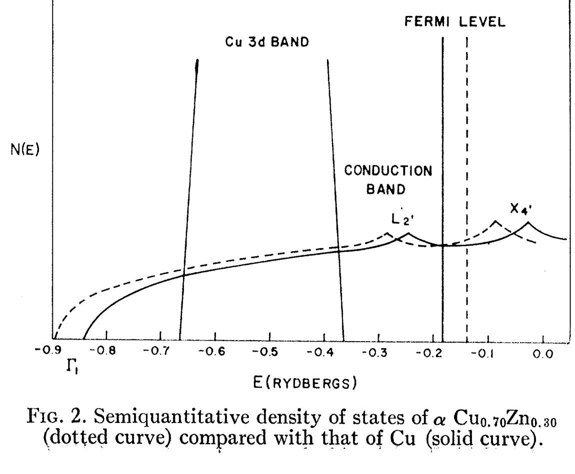

FIG. 2. Semiquantitative density of states of α $Cu_{0.70}Zn_{0.30}$ (dotted curve) compared with that of Cu (solid curve).

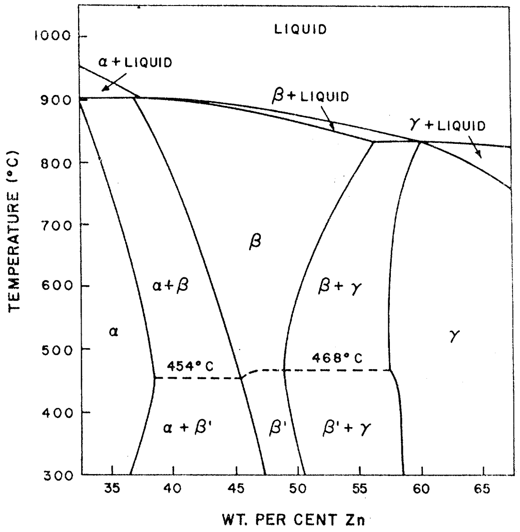

FIG. 3. Phase diagram of CuZn.

Thus as the energy gaps between the d bands and conduction states $(X_{4'},L_{2'})$ are reduced upon alloying, the corresponding peaks in the D.S. are shifted toward lower energies. On the other hand the Fermi level with respect to the Γ_1 state must increase in α CuZn as a result of adding one additional $4s$ electron per atom of Zn (notice: this shift in E_F is taken with respect to the shifted Γ_1). As implied above, the Fermi level is increased, and eventually ($\sim$45%) shifted into a region of decreasing D.S., where the alloy structure becomes unstable and assumes a new phase, the new phase being one which can support a larger Fermi surface with less expended energy. In Cu however, the Fermi surface already contacts the zone boundary at the hexagonal face centers (ΓL direction). As result of this, Hume-Rothery and Roaf[11] conjecture that when the Fermi surface increases in the ΓX direction (adding more electrons in the L direction would cost the energy of the gap as they would have to go in the second zone), the phase change might occur after contact of the Fermi surface with the square face centers. An experimental indication of this is suggested in the optical measurements of Biondi and Rayne and also those of Green.[22]

If the absorption peaks (see Biondi-Rayne[19]) are attributed to the d band–$X_{4'}$ transitions and the absorption edges to the d band–$L_{2'}$ transitions [i.e., in the vicinity of $k=(1,1,1)$], upon extrapolating the changes in these energies as Zn is added one notices that the Fermi surface crosses the square face centers at approximately 40% Zn or an electron to atom ratio of 1.4, which is the α-phase limit (see Fig. 3). (A similar interpretation of the optical data has been given by Lettington.[12])

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V. CONCLUSIONS

Our theoretical model of alpha brass is subject to a number of uncertainties. The "pseudo-periodic" approximation has, to date, only been applied to ideal one- and three-dimensional free-electron models, and is valid in these cases only to first-order perturbation theory. Actually, the energies $E(k)$ are formally complex, the imaginary part being associated with the diffuse scattering and lifetime of the Bloch wave function.[14] The effect of going to higher-order perturbation theory is to smear out the energy levels, effectively narrow the energy gaps, and cause the "tailing" of the density of states into the gap regions. It would be valuable to attempt a calculation of these effects in a real material.

Another uncertainty is the effect of alloying on the d bands. We have completely excluded such effects in our calculations because of the limitations of the "virtual-crystal" model. It is evident that the individual d bands of Cu and Zn ($M_{\text{II,III}}$ emission spectra) retain the forms characteristic of the pure metals.[23] However, it is impossible to infer from this data whether any shifts of the d bands relative to conduction bands occur as a result of alloying. Cohen and Heine[8] have suggested on the basis of Friedel's[9] theory that the Cu d band might be displaced to lower energy in the alloy. This is, of course, contrary to the present model and would require a somewhat different interpretation of the optical properties.

[*Note added in proof.* After submitting the manuscript, we became aware of an independent calculation of the electronic structure of alpha brass by Soven,[24] who has used Beeby's[15,16] t-matrix formulation for the density of states of a disordered alloy. However, Soven's final approximations involve: (1) the replacement of the actual averaged atomic t matrices by averaged pseudopotentials (based on the "muffin-tin" approximation) for the conduction states,[25] (2) the separation or partitioning of the conduction-electron and Cu d-electron secular problems, (3) the use of the Kohn-Rostoker-type structure constants in evaluating the Green's functions, and (4) the assumption of the rigid displacement of the Fermi level with respect to the bottom of the conduction band. These approximations are formally equivalent to the ones we have made in this paper in applying to first order the "pseudo-periodic" or "coherent-scattered-wave" model for disordered alloys originally introduced by Korringa[14] in 1958. One may compare Soven's calculated shifts in the peaks of the density of states as a function of quasi-momentum and atomic composition (see Fig. 8 of Ref. 24) with the level shifts indicated in Table I of this paper. The downward displacements of the $X_{4'}$ and $L_{2'}$ conduction levels are in almost exact agreement with those determined by Soven to 30% Zn concentration. However, our computed displacement of the L_1 level is more than twice that indicated by Soven. We do not understand the source of this discrepancy. Soven has taken an important step further in approximately establishing (to the accuracy of the first Born approximation) that the conduction states of alpha brass are well localized in momentum space, i.e., they are well represented by coherent or propagating Bloch waves. This, to a certain extent, encourages our use of the Korringa[14] statistical model of a disordered alloy. Moreover, Soven has been able to estimate the effects of alloying on the more localized Cu d bands. Stern[26] has recently emphasized the possible importance of charging effects in alloys. Such effects could be estimated theoretically in real alloys by carrying the Korringa-Kohn-Rostoker model to self consistency.[14] We should not expect charging to be too large for the conduction states of alpha brass because the amplitudes of the Cu and Zn wave functions are quite similar beyond the "muffin-tin" radii. The maintenance of the individual Cu and Zn d bands in the alloy is an extreme example of the charging effect associated with the more localized or core-like states.]

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[24] P. Soven, Phys. Rev. (to be published).

[25] This is essentially the adoption of the first Born approximation, in which the "phase shifts" of the Korringa-Kohn-Rostoker method are assumed equal to the matrix elements of the average "muffin-tin" pseudopotential. This procedure is strictly valid only if the partial-wave components of the conduction states are nearly free-electron-like.

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