Electronic Structure of IB-IIB Beta-Phase Alloys*

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Previous research on the theoretical electronic structure of ordered beta brass (β' CuZn) has been systematically extended to other ordered beta-phase alloys belonging to groups IB and IIB of the periodic table, and also to disordered beta brass (β CuZn). In the case of the ordered alloys, the band structures and Fermi surfaces of β' AgZn and β' AgCd have been computed by the Kohn-Rostoker (K-R) technique and compared with results similarly obtained for β' CuZn. The bands are qualitatively alike, differing principally in the locations of the d bands relative to the conduction bands. The sensitivity of these locations is given special attention in the material β' CuZn. The problem is partially resolved by resorting to a semiempirical "adjustment" of the d bands. The Fermi surfaces, which are close to the one-orthogonalized-plane-wave prototype, are relatively insensitive to the exact nature of the potential. The bands of β' AuZn and β' AuCd have not been calculated explicitly, although it is reasonable to assume that their electronic structures are basically similar to those of the Cu and Ag alloys. The optical properties of the β' alloys, including their variations with temperature and composition, are discussed on the basis of the computed bands. The bands and Fermi surface of disordered beta brass have been determined to first order of approximation by combining the K-R method with the "virtual-crystal" model. The electronic structure of β CuZn differs from that of β' CuZn in the following respects: The energy gap across the zone boundary is absent, corresponding to an absence of both the discontinuity in the Fermi surface across that boundary and the "holes" in the corners of the cube. The gap across each face of the dodecahedral zone boundary is reduced from 3.5 to 1.5 eV. Both these effects imply a somewhat more free-electron behavior for the disordered alloy. Finally, the bands are used to discuss the relative importance of electronic contributions and order to the stability of the beta-phase alloys.

I. INTRODUCTION

RECENT successful determinations of the band structure of several simple metals (e.g.,[1,2]) have stimulated our study of the IB-IIB binary alloys. The calculation of the electronic structure of the ordered alloy $Cu_{50}Zn_{50}$ was the first step in our investigation of the β-brass alloys. In this paper we present the extension of our work to other ordered alloys of the same family, and the results of preliminary calculations on disordered alloys.

Ordered beta brass (β'CuZn) is a traditional prototype binary alloy obeying the Hume-Rothery[3] rules. Its theoretical electronic band structure, Fermi surface, phase stability, optical, and other properties are the subjects of an earlier paper[4] [hereafter referred to as (I)] by two of the authors. In part II of this paper, analysis is extended to the class of IB-IIB ordered beta-phase alloys which include β'AgZn, β'AgCd, β'AuZn, and β'AuCd. As in (I), the Kohn-Rostoker[5] (K-R) or Green's-function method has been applied to the Ag alloys. The bands of the Au alloys have not been determined directly, because of the difficulty of properly including relativistic effects without a great deal of extra computational effort. Nevertheless, conjectures about their electronic structures may be made on the basis of

what is presently known about the electronic structure of Au.

The phase diagram of the CuZn alloy system is illustrated in Fig. 1. The β'(CsCl) structure disorders at high temperature to the β structure which is statistically bcc. This is also true of the AgZn and AgCd systems. However, no disordered phase has been observed below melting temperature in the cases of AuZn and AuCd. A great deal of attention has recently been directed to the theoretical problem of electronic structure in disordered systems. Fundamental questions have
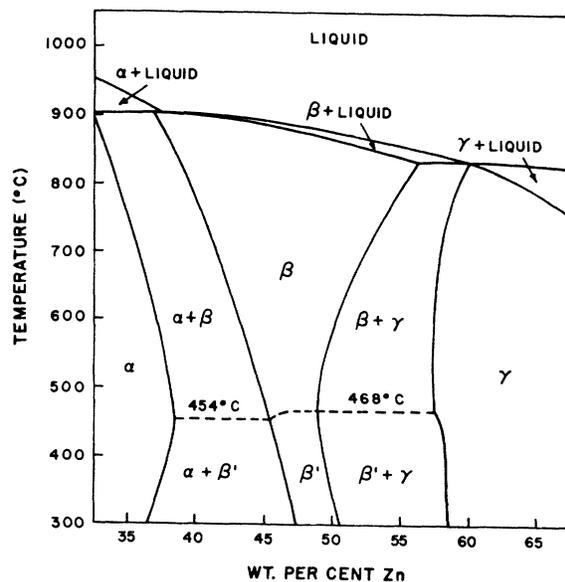
* Supported by the U. S. Atomic Energy Commission.

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

[1] B. Segall, General Electric Research Laboratory Report No. RL-2785G, 1961 (unpublished). Results for Cu published in Phys. Rev. 125, 109 (1962).

[2] L. F. Mattheiss, Phys. Rev. 134, A970 (1964).

[3] W. Hume-Rothery, J. Inst. Metals 35, 309 (1926).

[4] K. H. Johnson and H. Amar, Phys. Rev. 139, A760 (1965).

[5] W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).

Fig. 1. Phase diagram of the Cu-Zn alloy system.

FIG. 2. Comparison of several alternate crystal potentials for ordered beta brass based on modifications of free-atom potentials.
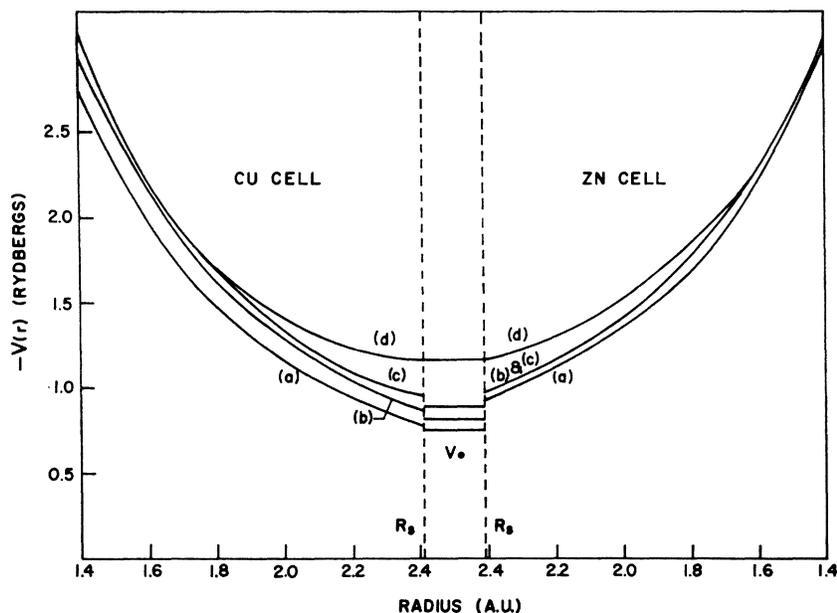
been raised as to the meaning of band structure and Fermi surface in such systems. Experimentally, we have good reason to believe that a band model is meaningful. We may cite, for example, the evidence of band gaps in disordered semiconductor alloys obtained by Johnson and Christian[6] and by Levitas, Wang, and Alexander.[7] Parmenter[8] has applied conventional perturbation theory through fourth order to obtain the band structures of both one- and three-dimensional models of disordered alloys. This work is particularly significant in that it justifies, to first order, Nordheim's[9] approximation of the "virtual crystal." In this approximation, one replaces the actual crystal potential appropriate to a particular arrangement of atoms in the alloy by its mean value over all possible random arrangements. The

effects of second order of perturbation are to narrow the gaps, smear the gap edges, and to cause the "tailing" of the density of states into the gap regions. More recent approaches to disordered alloys and liquid metals include the work of Korringa[10] (scattering-matrix method), that of Edwards[11] (infinite order perturbation theory), and that of Phariseau and Ziman[12] (Green's-function technique). Although these somewhat more

FIG. 3. Simple cubic Brillouin zone for ordered beta-brass type (β') alloys having the CsCl type of crystal structure. The basic symmetry points are shown.
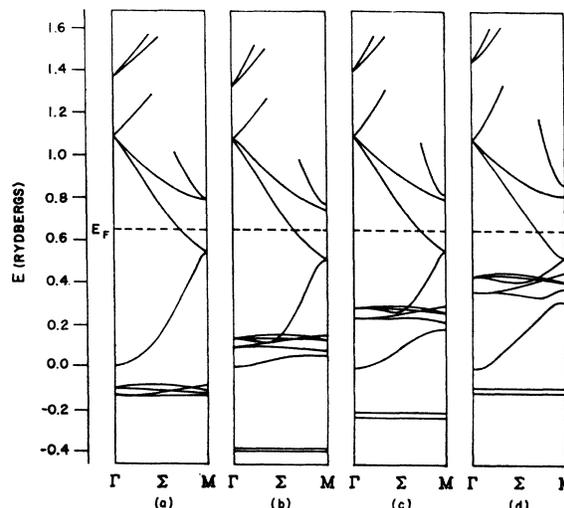
FIG. 4. Comparison of band profiles of ordered beta brass along the ⟨110⟩ (ΓΣM) direction of the zone resulting from the different crystal potentials shown in Fig. 2. The sensitivity of the relative position of d and conduction bands is clearly indicated.

[6] E. R. Johnson and S. M. Christian, Phys. Rev. 95, 560 (1954).
[7] A. Levitas, C. C. Wang, and B. H. Alexander, Phys. Rev. 95, 846 (1954).
[8] R. H. Parmenter, Phys. Rev. 97, 587 (1955).
[9] L. Nordheim, Ann. Physik 9, 607 (1931).
[10] J. Korringa, J. Phys. Chem. Solids 7, 252 (1958).
[11] S. F. Edwards, Proc. Roy. Soc. (London) A267, 518 (1962).
[12] P. Phariseau and J. M. Ziman, Phil. Mag. 8, 1487 (1963).
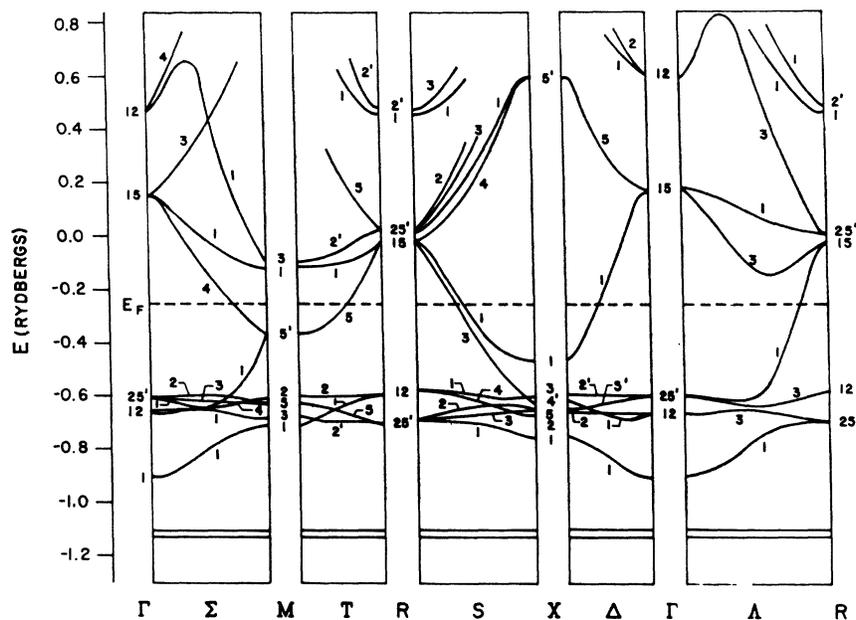
FIG. 5. Energy bands of β'CuZn.

sophisticated approaches differ as to calculational technique, they yield essentially the same physical interpretation for the alloy as that obtained by Parmenter.

One might hope, therefore, to obtain a first order approximation to the band structure of a real disordered alloy such as βCuZn by combining a "virtual-crystal" model for the potential with a standard calculational technique like the K-R method. This program has been carried out, and the results form the basis for part III of the present paper.

II. ORDERED BETA-PHASE ALLOYS

A. Sensitivity of the Bands to Choice of Potential

For the comparative study of the β'CuZn, β'AgZn, and β'AgCd band structures, it is important to have a consistent method of choosing the potentials. In (I) it was shown that the individual shapes of conduction and d bands and the derived Fermi-surface topology of β'CuZn are largely independent of small variations on the chosen crystal potential. In contrast, the relative positions of the d and conduction bands were shown to be quite sensitive to the exact nature of the potential. This is also true to the two Ag alloys.

The sensitivity can be explained in a straightforward fashion. The bands originating from the d and lower core electrons of the IB and IIB elements depend primarily on the nature of the corresponding potentials within a radius of 1 atomic unit (a.u.). Self-consistent, free-atom potentials are a reasonably accurate description of the fields experienced by these electrons at such radii. It is the behavior of the potential between 1 a.u. and the atomic-cell boundary which is most uncertain in the crystal because of the effects of correlation and

contributions due to neighboring atoms. The energies of the valence electrons, which give rise to the conduction bands, are very sensitive to variations of the potential in this region, and to any change of the chosen constant potential V_0 between muffin-tin spheres. One can literally shift the conduction bands relative to the d and core levels by merely altering the slopes of the potentials beyond a radius of 1 a.u. and/or adjusting V_0. This process is illustrated for several alternative potentials chosen in the case of β'CuZn (see Fig. 2). The resulting band profiles along the $\langle 110 \rangle$ ($\Gamma\Sigma M$) direction of the cubic zone (Fig. 3) are shown in Fig. 4. All energies in the latter figure are measured with respect to the Γ_1 level, effectively shifting the d bands with respect to the conduction bands.

It is difficult to arrive at a rigorously correct, yet practical, way of including both the contributions of correlation and neighbors. Electron-electron correlation screens the effect of exchange, making the potential less binding than in a pure Hartree-Fock treatment. Whether or not Slater's[13] approximation to the exchange constitutes a reasonable compromise is an unsettled issue. There are those who say its use still overemphasizes exchange at large radii,[14] and a screened version of it has been proposed.[15] There are those who take the exact opposite viewpoint.[16] Coulomb and exchange contributions from neighboring atoms can be described in terms of both spherical and nonspherical components about a given lattice site. The latter component is very

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[13] J. C. Slater, Phys. Rev. **92**, 603 (1953).

[14] F. Herman, J. Callaway, and F. S. Acton, Phys. Rev. **95**, 371 (1954).

[15] J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters **9**, 215 (1962).

[16] L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964).
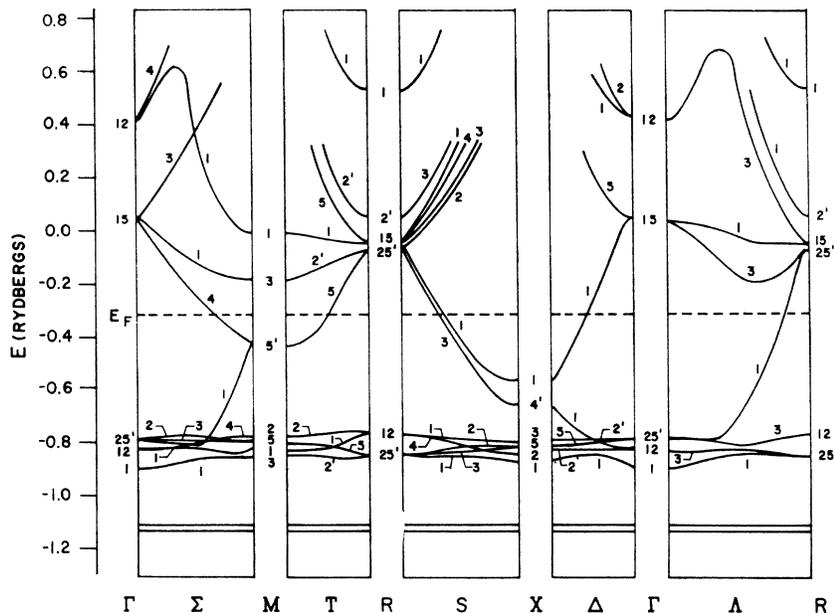
FIG. 6. Energy bands of β'AgZn.

small in cubic crystals. The spherical component tends to make the potential more binding. Methods of estimating the effects due to neighbors include renormalization of charge densities, the Löwdin[17] alpha-function expansion, and the Ewald[18] technique.

We have estimated a succession of such corrections in constructing the potentials of Fig. 2. The inconsistency of these potentials and the resulting bands in Fig. 4 suggest that it is perhaps better to rely on a semi-empirical method of fixing the relative positions of conduction and core bands in this series of alloys. The only observational data which can more precisely fix the d bands are those resulting from soft x-ray or optical experiments. Usable soft x-ray results are not available, to the authors' knowledge. However, Goldman and Muldawer[19] have recently extended optical measurements on β'CuZn into the near uv. Structural details in the absorption coefficient between 4.8 and 5.5 eV may be attributed to electronic transitions between the Cu $3d$ band and Fermi surface. Transitions involving the conduction bands are discussed in Sec. D.

We have, therefore, chosen as a basis for our calculations the Cu, Ag, Zn, and Cd self-consistent free-atom potentials originally constructed by Herman and Skillman[20] (H-S). They have the distinct advantage of having been computed in exactly the same manner for each element. The H-S potentials for Cu and Zn are the ones in Fig. 2 marked with the letter (b). The d bands of β'CuZn have then been adjusted upward relative to the conduction bands by 0.15 Ry and their width in-

creased slightly to agree with the measured optical properties. Lacking measurements into the uv for the Ag alloys, we have made the same relative adjustment in the cases of β'AgZn and β'AgCd. However, the Ag $4d$ bands in these alloys consistently lie lower than the Cu $3d$ bands in brass (see the following section).

B. The Band Profiles

The band profiles of β'CuZn, β'AgZn, and β'AgCd are plotted, respectively, in Figs. 5, 6, and 7 along the principal symmetry directions of the zone. The bands of β'CuZn are essentially the same as those described in Fig. 7 of (I). The results for the silver alloys are strikingly similar to those for beta brass. The conduction bands are quite free-electron in shape, although energy gaps at high-symmetry points, e.g., $X_{4'}$-X_1, $M_{5'}$-M_1, and $R_{25'}$-R_1, tend to be larger than those customarily found in simple metals like the alkalis Zn and Al. In each material the conduction band is cut by a fairly narrow d band arising from the IB element. Below the conduction band is a very narrow d band originating from the IIB element (illustrated with two parallel lines). The Ag $4d$ band in both alloys is positioned approximately 0.2 Ry (2.7 eV) lower with respect to the conduction band than is the Cu $3d$ band of βCuZn. A similar difference has been computed by Segall[1] in the cases of pure Cu and Ag.

C. The Fermi Surfaces

The determination of the Fermi levels has been discussed in (I). They are indicated by the dotted lines in Figs. 5 through 7. The intersection of the Fermi level with the band profile allows an approximate mapping of important cross sections of each Fermi surface. The

[17] P. O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 96.
[18] P. Ewald, Ann. Physik **49**, 117 (1916).
[19] H. Goldman and L. Muldawer (private communication).
[20] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood, New Jersey, 1963).
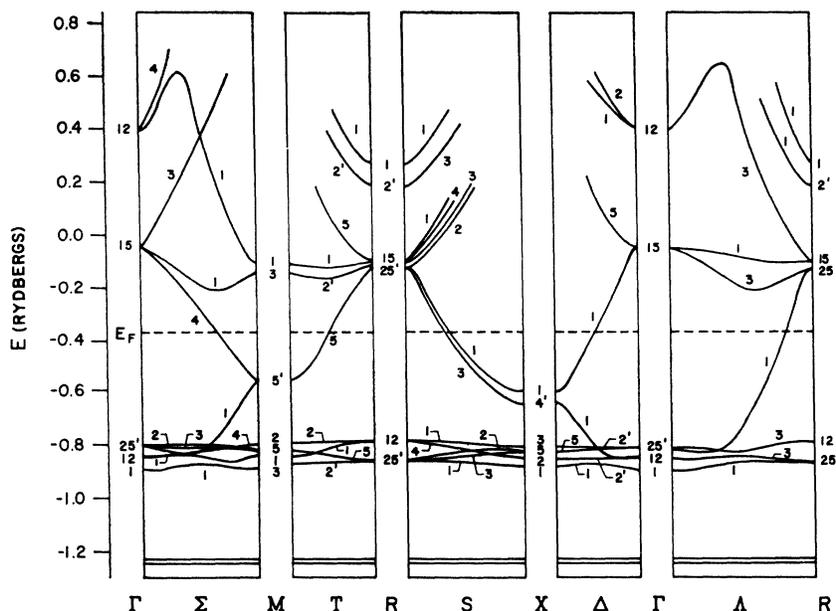
FIG. 7. Energy bands of β'AgCd.

Fermi surfaces of the three alloys are similar. They can be generated by a slight distortion of the one-orthogo-nalized-plane-wave (1-OPW) prototype. The first (cubic) zone (see Fig. 3) exhibits hole-like behavior in the corners. The second (dodecahedral) zone (see Fig. 8) is slightly more than half full with measurable contact of the Fermi surface at the 12 faces of the dodecahedron. In Fig. 9 we have sketched a {110} cross section of the Fermi surface of β'CuZn in the extended-zone scheme. The first two zones are included. The holes are plainly visible. The gap across the cubic zone bound-ary, namely, S_3-S_1 and $X_{4'}$-X_1 in Fig. 5, gives rise to

the discontinuity in the Fermi surface between zones. The presence of "necks" whose axes are along the $\langle \Gamma\Sigma M \rangle$ direction is associated with the contact of the Fermi surface at the faces of the second zone.

The theoretical Fermi surface of ordered beta brass is in good agreement with that discussed by Springford et al.[21] on the basis of de Haas–van Alphen data. A comparison of theoretical cross-sectional areas of the "hole orbits" and "neck orbits" with the experimental values is carried out in Table I. Theoretical values are
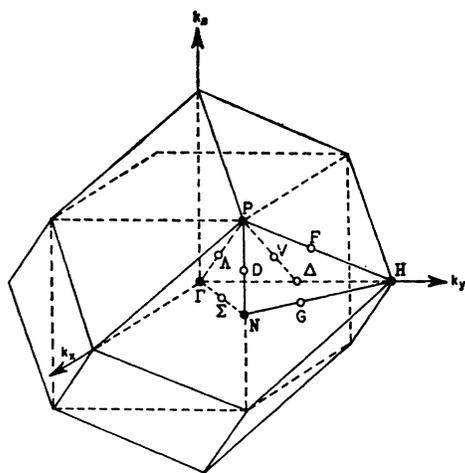
FIG. 8. Dodecahedral Brillouin zone for disordered beta-brass type (β) alloys having the statistical bcc crystal structure. The basic symmetry points are shown. The cubic zone (dotted lines) may be taken as a reduced zone. The dodecahedron also repre-sents the second zone for the ordered alloys in the extended-zone scheme.
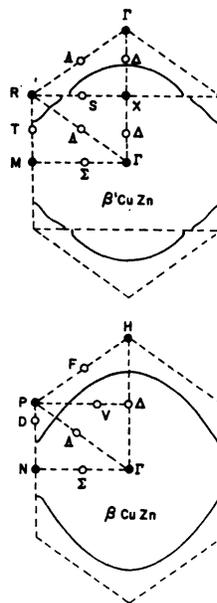
FIG. 9. {110} cross sections of the theoretical Fermi surfaces for ordered and disordered beta brass, respec-tively. The extended-zone scheme is used.

[21] M. Springford, W. B. Pearson, J. P. Jan, and I. M. Templeton (private communication).

TABLE I. Theoretical cross-sectional areas of {110} "hole orbits" and "neck orbits" of ordered and disordered beta-brass-alloys. Experimental results for β'CuZn included. Unit of area is that of cubic zone face.

	"Hole orbit"	"Neck orbit"
β'CuZn (Theor.)	0.0830±.007	0.19±0.02
β'CuZn (Expt.)	0.089[a]	0.17[b]
βCuZn (Theor.)	none	0.11±0.02
β'AgZn (Theor.)	0.11 ±0.02	0.16±0.03
β'AgCd (Theor.)	0.13 ±0.02	0.20±0.03

[a] M. Springford, W. B. Pearson, J. P. Jan, and I. M. Templeton (private communication).
[b] M. Springford (private communication).

also included for the cases of β'AgZn and β'AgCd. Springford[22] is presently applying the de Haas–van Alphen method to these alloys.

D. Optical Properties

The normal-incidence reflectivities of the IB-IIB β' alloys over the visible part of the spectrum and as a function of temperature have been reported by Muldawer.[23] The reflectivities at room temperature (including those of β'AuZn) are compared in Fig. 10. A minimum in the vicinity of the wavelength 5000 Å is clearly present for each specimen. The relative sharpness and spectral energy of this minimum decreases through the sequence β'CuZn → β'AgZn → β'AuZn → β'AgCd. The reflectivity of ordered beta brass at high temperature is compared with that at room temperature in Fig. 11. The effect of temperature is to unsharpen the reflectivity minimum and to displace its position to lower energy. A similar behavior is observed in each of the other alloys.

In (I) it has been proposed that the reflectivity minimum of β'CuZn is associated with the onset of electronic transitions at an energy of 2.5 eV between the Fermi surface (at levels $\Sigma_{4'}$ and T_5) and the overlying levels
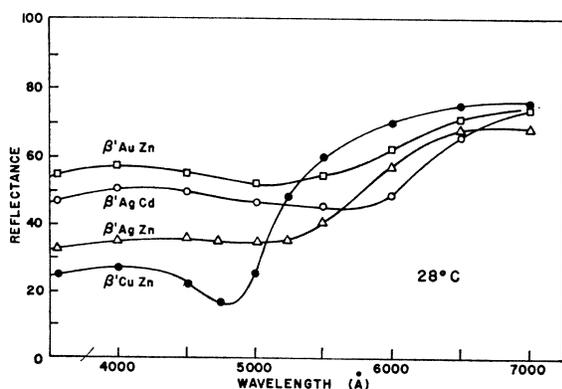
FIG. 10. Comparison of the normal-incidence spectral reflectivities of the ordered beta-brass type alloys measured at room temperature (see footnote 23).

[22] M. Springford (private communication).
[23] L. Muldawer, Phys. Rev. 127, 1551 (1962).
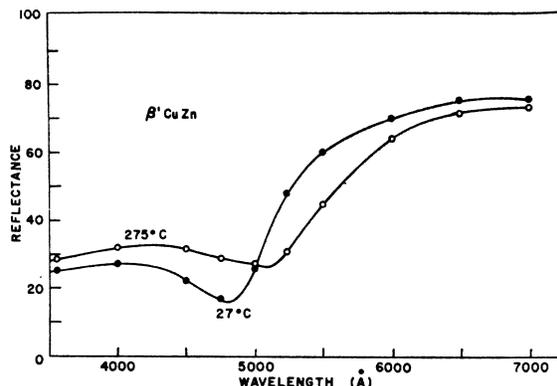
FIG. 11. Comparison of normal-incidence spectral reflectivity of ordered beta brass measured at room temperature with that measured at high temperature (see footnote 23).

Σ_1 and T_1 (see Fig. 5). The similarity of the bands of β'AgZn and β'AgCd suggests that the same type of transitions are responsible for the reflectivity minima of these materials. We have listed in Table II the theoretical energy gaps along with the spectral energies of the room-temperature reflectivity minima. The agreement is good, except for the above-mentioned trend of the minima to lower energies.

Both the crystal volume and the relative excitation of lattice vibrations are functions of temperature. The one-electron energy levels and their gaps can, therefore, suffer shifts as a consequence of these effects. The band profiles in Figs. 5–7 are valid only for a temperature of absolute zero. The effect of lattice expansion can be determined by computing important band gaps as a function of lattice constant. This is easily accomplished with the K-R method. We have carried this out and found a reduction of only about 10^{-5} eV/°C for each gap. The effect due to lattice vibrations is more of a problem. In principle, time-dependent perturbation theory can be used. In practice, one cannot evaluate the perturbation summations because of a lack of knowledge of the electron-phonon matrix elements and of the spectrum of intermediate states. A few semiquantitative approximations have been proposed for different classes of materials. These include Fan's[24] approximation for

TABLE II. Theoretical energy gaps, spectral energies of reflectivity minima, and Debye temperatures of ordered beta-brass-type alloys. Energies are in eV and Debye temperatures are in °K.

	$\Sigma_{4'}(E_F) \to \Sigma_1$	$T_5(E_F) \to T_1$ (or $T_{2'}$)	Refl. min.[a]	Debye temp.[a]
β'CuZn	2.5±0.1	2.6±0.1	2.48	252
β'AgZn	2.4±0.2	2.5±0.2	2.18	215
β'AuZn	not computed	not computed	2.07	192
β'AuCd	not computed	not computed	2.07	164
β'AgCd	2.4±0.2	3.0±0.2	2.03	174

[a] L. Muldawer, Phys. Rev. 127, 1551 (1962).

[24] H. Y. Fan, Phys. Rev. 78, 808 (1950).

FIG. 12. Energy bands of disordered beta brass. Conduction bands are based on the virtual-crystal approximation.

semiconductors and Edwards'[11] approximation for simple metals. All predict a decrease in gap width and a broadening of gap edges, each to the order of 10^{-3}–10^{-4} eV/°C. The displacement with temperature of the reflectivity minimum in Fig. 11 is almost 5×10^{-4} eV/°C. Thus the dominant contribution to the temperature effects in the beta-brass-type alloys may very likely be attributed to the results of lattice vibrations or electron-phonon interaction.

Differences in the lattice spectra for various materials are measured by the Debye temperatures. In Table II we have included a list of mean Debye temperatures for the alloys. The trend of these temperatures to lower values through the sequence $\beta'\mathrm{CuZn} \to \beta'\mathrm{AgZn} \to \beta'\mathrm{AuZn} \to \beta'\mathrm{AgCd}$ matches the trend of the reflectivity minima to lower energies. It is evident that some decreasing function of the Debye temperature, say (T/Θ_D), may be related to the relative decrease in gap width and to the unsharpening effects observed for each alloy.

Electron-phonon interaction and the breakdown of selection rules are intimately related. The decrease in gap width and broadening effects may equally well be attributed to the presence of nondirect interband transitions. Berglund and Spicer[25] have discussed the importance of nondirect transitions in the noble metals.

III. DISORDERED BETA BRASS

A. The Virtual-Crystal Approximation

We have attempted a first-order calculation of the band structure of disordered beta brass (βCuZn) by

adopting a virtual-crystal model for the conduction bands. That is, the $4s$ electrons of Cu and Zn are assumed to experience an average potential near each lattice site given by

$$\langle V(r) \rangle_{\mathrm{av}} = (1-C)V(\mathrm{Cu}) + CV(\mathrm{Zn}) , \qquad (1)$$

in which $V(\mathrm{Cu})$ and $V(\mathrm{Zn})$ are respectively the H-S free-atom potentials. The concentration C may be varied over a range of compositions covering the β field. The calculation was carried out with the K-R method, using the structure constants for a simple bcc lattice tabulated by Segall and Ham.[26]

The $3d$ electrons, as usual, pose something of a problem. Should we consider those originating from Cu and those originating from Zn to give rise to an average $3d$ band? Or shall we consider each to give rise to a characteristically individual and narrow band similar to those of the ordered alloy? The former choice would imply that the d electrons in the crystal overlap considerably and have the same degree of freedom as do the conduction electrons. The latter choice would emphasize the core nature of the d electrons.

It has been argued that the d electrons of transition and noble metals do indeed experience a moderate degree of overlap and contribute to cohesion. This is also likely true of the d electrons in the IB-IIB alloys, except to a smaller degree because of lower and more narrow configuration of the d bands relative to the conduction bands. Regardless of this partial freedom, which is difficult to describe quantitatively, the dominant role of the d electrons in the crystal is as constituents of the ion cores. There is soft x-ray evidence which supports

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

[26] B. Segall and F. S. Ham, General Electric Research Laboratory Report No. 61-RL-(2876G), 1961 (unpublished).

this contention. Clift, Curry, and Thompson[27] have observed in both Cu-Zn and Ni-Cu alloys that the emission spectra retain forms characteristic of the individual metals. It is interesting to note also that in treating a hypothetical one-dimensional alloy, Parmenter[8] has found that the virtual-crystal approximation breaks down in the case of well localized wave functions characteristic of the separate alloy constituents. On the basis of these considerations, we have adopted the viewpoint that in disordered beta brass Cu and Zn form individual d bands similar to those of the ordered alloy.

B. The Band Profiles

The bands have been computed for the high-symmetry points of the dodecahedral zone shown in Fig. 8. The cubic zone, indicated by the dotted lines, may be taken as a reduced zone for the bcc lattice along the $\langle 100 \rangle$ direction. Those sections of the bands between $\mathbf{k} = (2\pi/a)(\frac{1}{2},0,0)$ and $\mathbf{k} = (2\pi/a)(1,0,0)$ can be folded into the cube, yielding twice as many bands between $\mathbf{k} = (2\pi/a)(0,0,0)$ and $\mathbf{k} = (2\pi/a)(\frac{1}{2},0,0)$. Because the atoms are statistically identical in the completely disordered alloy, bands having the same symmetry properties should meet at common points on the cubic zone boundary. One-to-one comparisons may be made between symmetry points of the dodecahedron and those of the cube. At some points the symmetry groups are identical, e.g., H and Γ, G and Σ, F and Λ. In other cases, the group of the point for the dodecahedron is a simple subgroup of that for the corresponding point of the cube, e.g., N and M, D and T, P and R, V and S.

Utilizing the reduced-zone scheme and these correspondeces, we have plotted in Fig. 12 the bands of disordered beta brass for the composition $\beta Cu_{50}Zn_{50}$. They may be compared readily with the results of ordered beta brass shown in Fig. 5. The most obvious effect of disorder is the disappearance of the gap across the cubic zone boundary. Replacing the gap is a doubly degenerate V_+ band and the Δ_1 bands which touch at the center of the cube faces. This behavior is related to the disappearance of the superlattice lines due to the {100} Bragg planes of reflection in the x-ray analysis of the order-disorder transformation. The 1.5 eV $N_{1'}$-N_1 gap across each face of the dodecahedron may be compared with the 3.5 eV $M_{5'}$-M_1 gap for the ordered alloy. Both are p-s gaps with respect to the nodal structure of their first nonvanishing wave-function components. The reduction of the gap reflects the tendency of $\beta CuZn$ to be even more free-electron-like than $\beta'CuZn$.

The bands at other symmetry points of the respective zones may be compared. For example, the $H_{15}(p)$ and $H_{12}(d)$ conduction levels of $\beta CuZn$ are in the same order and approximately same energy range as the $\Gamma_{15}(p)$ and $\Gamma_{12}(d)$ levels of $\beta'CuZn$. The $G_4(p)$ and $G_1(s)$ bands

[27] J. Clift, C. Curry, and B. J. Thompson, Phil. Mag. **8**, 593 (1963); **8**, 639 (1963).
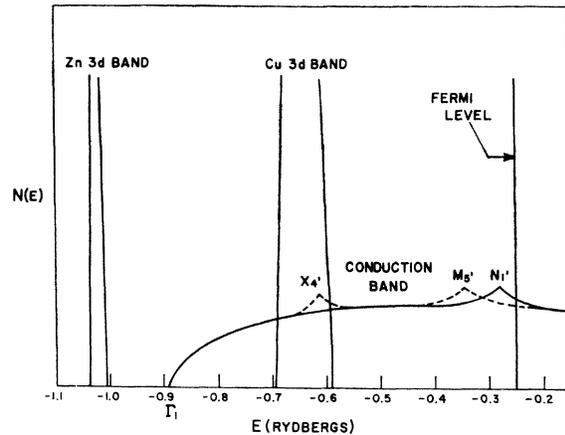
FIG. 13. Semiquantitative density of states of disordered beta brass (solid curve) compared with that of ordered beta brass (dotted curve).

which connect H_{15} with $N_{1'}$ and N_1, respectively, are similar to the $\Sigma_4(p)$ and $\Sigma_1(s)$ bands which join Γ_{15} to $M_{5'}$ and M_1, respectively. The $D_3(p)$ and $D_1(s)$ bands connecting $P_4(p)$ with $N_{1'}$ and N_1 correspond to the $T_5(p)$ and $T_1(s)$ bands connecting $R_{15}(p)$ with $M_{5'}$ and M_1. The $F_1(S)$ and $F_3(p)$ bands between H_{15} and P_4 are similar to the $\Lambda_1(S)$ and $\Lambda_3(p)$ bands between Γ_{15} and the two levels $R_{25'}$ and R_{15}. Despite differences between the formal symmetry levels for the bands of ordered and disordered beta brass, the fundamental nodal structures of the associated wave functions and the ordering of energy bands are essentially the same in both materials.

We have computed the $N_{1'}$-N_1 band gap as a function of composition by varying the concentration C in Eq. (1) at steps of 6% over the range $\beta Cu_{56}Zn_{44}$—$\beta Cu_{44}Zn_{56}$. The change in the gap was found to be negligible.

C. The Fermi Surface

We have compared in Fig. 9 a {110} cross section of the theoretical Fermi surface of $\beta CuZn$ with that of $\beta'CuZn$. The discontinuity of the surface across the cube and the "hole orbits" are absent in the former case. The reduction of the energy gap across the dodecahedral zone boundary leads to a reduction in the cross section of the "neck orbit," also evident in Fig. 9. In Table I we have included the pertinent theoretical Fermi-surface data of $\beta CuZn$ so that it may easily be compared with the theoretical and experimental data for the ordered alloys. The Fermi surface of disordered beta brass is more nearly spherical than that of the ordered alloy. One may presume this is also true of $\beta AgZn$ and $\beta AgCd$.

IV. BETA-PHASE STABILITY

The electron-to-atom ratio at the eutectoid point of disordered beta brass is 1.468 (see Fig. 1). This is close

to the value of 1.48 predicted by Jones[28] on the basis of the free-electron model. The agreement is not surprising in view of the nearly free-electron behavior of the alloy. Mott and Jones[29] originally suggested that a transformation from one alloy phase to another is favorable when the Fermi level is in a region of falling density of states. Semiquantitative densities of states for both βCuZn (solid curve) and β'CuZn (dotted curve) are plotted in Fig. 13. The density peaks near the energy level $N_{1'}$ (see Fig. 12) in the case of disordered alloy. Contact of the Fermi surface with the dodecahedral zone boundary places E_F on the side of falling $N(E)$. Thus the condition of βCuZn is theoretically favorable for a phase transformation, in agreement with the observed β-γ phase boundary of Fig. 1.

Since the band structures and Fermi surfaces of the ordered alloys β'AgZn and β'AgCd are similar to those of ordered beta brass, we would expect that calculations on the disordered Ag alloys by the virtual-crystal model would yield correspondingly similar results to those of disordered beta brass. This would suggest, in turn, that the explanation of the stability for βAgZn and βAgCd should follow closely that given above.

Contact of the Fermi surface with the dodecahedral (second) zone boundary is larger in the case of β'CuZn. Consequently, E_F lies even farther beyond the peak in $N(E)$ which occurs at the energy level $M_{5'}$. The explanation of the stability of this alloy is complicated by the presence of order, which reveals itself by the peaking of $N(E)$ near the $X_{4'}$ level. The ordering energy is most likely related to a small net ionicity of the IB and IIB atoms in the alloy [see discussion in (I)]. Order, rather than electronic considerations, may actually be the dominant factor in determining the stability of the β' alloys.[30] This may explain why no disordered beta phases of AuZn and AuCd have been observed below melting temperature.

V. CONCLUSIONS

A systematic application of the K-R method combined with a series of potentials based on the free atoms have permitted a computation of band structures and Fermi surfaces for a series of IB-IIB beta-phase alloys.

[28] H. Jones, Proc. Phys. Soc. (London) 49, 243 (1937).
[29] N. F. Mott and H. Jones, The Theory of the Properties of Metals and Alloys (Dover Publications, Inc., New York, 1958).
[30] This viewpoint has also been expressed by J. Friedel, Nuovo Cimento Suppl. 7, 287 (1958) and by T. B. Massalski and H. W. King, Progress in Materials Science, edited by B. Chalmers (Pergamon Press, New York, 1961), Vol. 10, p. 44.

The ordered alloys β'CuZn, β'AgZn, and β'AgCd exhibit a degree of free-electron behavior somewhere between that characteristic of the alkalis and polyvalent metals and that characteristic of the transition and noble metals. The bands of β'AuZn and β'AuCd have not been computed explicitly. Nevertheless, we may speculate that their electronic structures are at least qualitatively similar to those of the other alloys. The uniformity of the optical properties and ranges of composition stability strengthen this viewpoint. The chief uncertainty in the results for the ordered alloys is the location of d bands with respect to conduction bands. The optical properties are not conclusive in this respect. An independent check by soft x-ray method would be helpful. We can be reasonably certain, however, that the relative difference (of 0.2 Ry) between the locations of d bands in the Cu and Ag alloys is preserved regardless of their absolute positions. From what is presently known about pure Au[31] we may assume that in β'AuZn and β'AuCd the d bands are more like those of β'CuZn than those of the Ag alloys.

The theoretical band structure and Fermi surface computed for disordered beta brass are, of course, subject to several uncertainties. First, we have adopted in the virtual-crystal approximation a straightforward, but admittedly, oversimplified treatment of the conduction bands. The smearing out of the energy levels, effective narrowing of the energy gaps, and "tailing" of the density of states into the gap regions, all predicted to second order of perturbation theory, have been neglected. Furthermore, we have not considered the possible effects of disorder, small as they may be, on the positions and widths of the Cu and Zn d bands. Finally, decisive experimental tests are lacking. The topological type of experiment, such as the de Haas–van Alphen method, which has proven so useful in the cases of simple metals and ordered alloys, is not presently applicable to the disordered beta-phase alloys.

ACKNOWLEDGMENTS

[31] B. R. Cooper and H. Ehrenreich, Bull. Am. Phys. Soc. 10, 111 (1965).