FURTHER BAND THEORY ARGUMENTS ELUCIDATING THE NATURE OF THE ORDERED STATE OF THE CsCl TYPE ALLOY β'-CuZn

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Partial wave analysis together with the qualitative analysis of hybridization in β'-CuZn is used to shed more light on special bonding conditions in which stability of this phase might originate. Results support the legitimacy of the so-called polar model of this phase. Analogy to the ordered Cu_3Au alloy is mentioned, the difference being that the latter stabilizes due to a pure super-structure effect. Shockley surface states found recently on the (111) surface of Cu_3Au are to be expected on the same face of α-CuZn as well.

Recent investigations[1-4] of a number of CsCl (B2) type alloys including CuZn, from the point of view of the so-called qualitative theory[2,5] of Shockley surface states, revealed interesting qualitative conclusions on the importance of covalency and ionicity in the binding mechanism of these alloys, as well as on the role which these two components of bonding can have in the formation and stability of the ordered phase. The arguments were based on a systematic analysis of pronounced gaps in the band structure, especially those lying near the Fermi energy E_F, with particular emphasis on the character of bonding for which they might be responsible. According to the qualitative theory, a gap in the solid can be either hybridizational (HG) or non-hybridizational (NHG). We refer the reader to refs[2,5] for the definition. According to refs[1-3], a HG is related to the chemical bonding (covalency), especially if it is located around E_F and separates the bonding states from the antibonding ones, whereas an NHG can be related to the ionicity if favourable conditions are fulfilled (see below). Naturally, in alloys covalency and ionicity can survive only as a residual (or fringe) effect. However, and that was the main point in refs[1-3], in the neighbourhood of the disorder-order phase transition, they can become more pronounced and start to operate as a triggering mechanism of the transition. Contrary to the metallic bonding, they are the only bonding characteristics that change in the neighbourhood and in the course of the phase transition. On the other hand, such an electronically driven transition usually occurs if this change in the bonding mechanism produces a pronounced dip in the density of states $n(E)$ of the ordered phase near E_F since then the ordered structure can be energetically more favourable than the disordered one.

Application[1-4] of the above strategy to various B2 type alloys has shown that two pronounced dips in $n(E)$, differing in the character of hybridization, are important for our considerations. At the same time, B2 alloys appeared to be split into two

distinct groups quite different in their stability, according to whether the Fermi level E_F fell into the lower or the upper dip, respectively. The first group (lower dip) comprises alloys like FeAl and CoAl. For the second group (upper dip), CuZn is the best known representant. Qualitative analysis has shown that for the lower dip, an (sp, e_g) and an (sp, t_{2g}) HG are responsible in both groups of alloys. The upper dip in the first group derives from the (sp, t_{2g}) HG. Similar conclusion has been also reached for the upper dip of the second group in ref.[2], where partial wave analysis of ref.[6] has been used which is incomplete at energies above E_F. However, the analysis[3] of trends based on more recent data[7,8] revealed that no strong (sp, t_{2g}) hybridization should be involved in the upper dip of CuZn. A part of the present new data on partial wave analysis which can be found in the text (Tables I–III), provides a solution of this question and helps also to clarify the nature of bonding and ordered phase stability in CuZn. To enable more detailed comparison with refs[4-6], results on the presently calculated partial wave analysis can be found in Tables IV, V. The whole partial wave analysis has been performed for the β′-CuZn band structure of ref.[9] which does not deviate too much from that of refs[6,10]. Our partial wave analysis results resemble those of ref.[6]. There is a difference between the band structure of refs[9,11] in the position of Zn 3d band deep below E_F which can at best introduce a HG unimportant here.

RESULTS

The Σ_1 States

The absence of the (sp, t_{2g}) hybridization in the upper dip is clearly seen from Table I showing the behaviour of partial (s, p, d) charges along the Σ direction. The critical upper dip gap encompassing the Fermi energy $E_F = 0.59$ Ry*, is delimited from above by the $\Gamma_{15} - \Sigma_1 - M_3$ (upper) branch and from below by the $\Gamma_{25'} - \Sigma_1 - M_5$, branch. At energies below E_F, a broad $(s$ or $p, t_{2g})$ HG lying between the $\Gamma_{25'} - \Sigma_1 - M_5$, and the $\Gamma_1 - \Sigma_1 - M_3$ (lower) branches exists, into which a narrow $\Gamma_{12} - \Sigma_1 - M_1$ band of e_g character is immersed.

Our interpretation of the band structure rests on the assumption, that it follows from the interaction of the originally non-interacting non-hybridized branches $\Gamma_1 - \Sigma_1 - M_3$ (upper) of s character, $\Gamma_{15} - \Sigma_1 - M_5$, of p character, $\Gamma_{25'} - \Sigma_1 - M_3$ (lower) of t_{2g} character and $\Gamma_{12} - \Sigma_1 - M_1$ of e_g character. The crossings of these branches lead to the opening of HG (the so-called non-crossing rule). In comparison with aluminides (FeAl, CoAl), the (sp, t_{2g}) hybridization moves to lower energies with respect to E_F. This is clearly seen from the fact that M_3 (upper) in CuZn has s character, while in aluminides the d character is strong (compare Table I

TABLE I

Partial wave analysis for four energy branches delimiting the gaps in Σ_1 states. Irreducible representations (IR), energy (E) from ref.[9] and the percentage of the wave function character (C) in muffin-tin (Cu or Zn) spheres. The „missing" charge (up to 100%) falls essentially outside the muffin-tin spheres. $E_F = 0.59$ Ry for β'-CuZn ($cf.$ also Table X of ref.[4])

Point:	Γ	Σ (middle)	M
IR	15	1	3
E(Ry)	1·0645	0·8063	0·6985
C(Cu) %	26·899p	19·201s	37·171t_{2g}
		13·392d^a	
		5·327p	
C(Zn) %	42·145p	21·498s	48·061s
		11·708p	2·471e_g
		5·987d	
IR	25′	1	5′
E(Ry)	0·3633	0·3326	0·4717
C(Cu) %	97·791t_{2g}	93·231d	24·777p
		1·125s	
		0·163p	
C(Zn) %	0·950t_{2g}	2·139p	36·617p
		0·245d	
		0·021s	
IR	12	1	1
E(Ry)	0·2977	0·2998	0·3117
C(Cu) %	91·337e_g	89·153d	87·830e_g
		0·716s	2·532s
		0·359p	
C(Zn) %	2·672e_g	1·808d	3·280t_{2g}
		1·281p	
		0·980s	
IR	1	1	3
E(Ry) %	−0·1351	0·0282	0·2269
C(Cu) %	26·957s	18·877s	68·006t_{2g}
		5·620p	
		1·645d	
C(Zn) %	40·385s	33·411s	18·290s
		6·421p	3·837e_g
		2·543d	

^{a} $d = e_g + t_{2g}$.

of the present work, ref.[3] and the discussion to Table X in ref.[4]). However, it is obvious from Table I, that in CuZn M_3 (upper) is still appreciably influenced by the interaction with t_{2g} states. The critical upper gap results from strongly mixed s and p states with Cu and Zn atoms equally involved so that the division into non-interacting s and p branches is based largely on intuition.

The Δ_1 and Λ_1 States

According to Table II, in the Δ_1 states below E_F one identifies an (sp, e_g) HG which derives from two non-interacting branches, namely, the $\Gamma_{12} - \Delta_1 - X_1$ branch of e_g character and the sp Δ_1 branch starting in Γ_{15}.

Table III shows that in Λ_1 states below E_F an (sp, t_{2g}) HG exists which is caused by the crossing of the non-interacting $\Gamma_{25'} - \Lambda_1 - R_{25'}$ branch of t_{2g} character and the $\Gamma_1 - \Lambda_1 - R_2$ branch of sp character. One can see from ref.[3] and from the discussion of Table IX of ref.[4] that analogous HG exist also in aluminides.

TABLE II

Partial wave analysis for two energy branches delimiting the HG in Δ_1 states (cf. also Table VII of ref.[4])

Point:	Γ	Δ (middle)	X
IR	15	1	1
E(Ry)	1·0645	0·6668	0·4247
C(Cu) %	26·899p	13·588e_g	77·036e_g
		13·005p	10·016s
		10·542s	
C(Zn) %	42·145p	22·548p	6·316p
		10·363s	
		3·285e_g	
IR	12	1	4'
E(Ry)	0·2977	0·3018	0·1881
C(Cu) %	91·337e_g	85·012e_g	16·443p
		1·728p	
		0·224s	
C(Zn) %	2·672e_g	2·665e_g	47·815s
		1·901p	7·190e_g
		1·360s	

The comparison of the behaviour of the partial wave analysis along the Σ, Δ and Λ directions reveals the following conclusion important for a better understanding of the nature of hybridization in B2 type alloys. As compared with aluminides (FeAl, CoAl), the energy levels of CuZn lying in the neighbourhood of E_F and above it suffer a depletion in d-states as can be seen by looking at M_3 (upper) in Table I and the point X_1 in Table II of the present work, and the discussion and Table VII of ref.[4]. At the same time, CuZn levels further below E_F are enriched in d-states as follows, *e.g.* from results for Γ_{12}, $\Gamma_{25'}$ in Tables I and II of the present work and Tables VII and IX of ref.[4].

These facts justify the general conclusion reached in ref.[3] that with B2 type alloys, the above effect can be observed when E_F moves upwards in the band structure. (This represents a deviation from the „rigid band" model based on the same band structure for all members of a given family of alloys and differing only in the position of E_F.) They justify the viewpoint[1-4,12] advocated also in the present paper, namely, that the gap critical for the phase transition with aluminides (the lower gap) arises

TABLE III

Partial wave analysis for two energy branches delimiting the HG in Λ_1 states (*cf.* also Table IX of ref.[4])

Point:	Γ	Λ (middle)	R
IR	$25'$	1	$2'$
$E(Ry)$	0·3633	0·3523	0·8728
$C(Cu)\,\%$	$97\cdot791\,t_{2g}$	$86\cdot969\,t_{2g}$	—
		$3\cdot883\,s$	
		$0\cdot685\,p$	
$C(Zn)\,\%$	$0\cdot950\,t_{2g}$	$2\cdot561\,p$	$86\cdot650\,s$
		$1\cdot754\,t_{2g}$	
		$0\cdot087\,s$	
IR	1	1	$25'$
$E(Ry)$	$-0\cdot1351$	0·0979	0·2664
$C(Cu)\,\%$	$26\cdot957\,s$	$14\cdot206\,p$	$82\cdot566\,t_{2g}$
		$7\cdot834\,t_{2g}$	
		$7\cdot054\,p$	
$C(Zn)\,\%$	$40\cdot385\,s$	$30\cdot936\,s$	$8\cdot913\,p$
		$8\cdot406\,p$	
		$1\cdot502\,t_{2g}$	

due to a strong (sp, d) hybridization, while with β'-CuZn (the upper gap) such a situation is missing.

DISCUSSION

Numerical data of the present work have provided additional insight into the character of the critical upper gap at E_F and the nature of bonding in the ordered state of β'-CuZn. The conclusions reached at are the following:

a) Contrary to aluminides, the above gap does not exhibit strong (sp, t_{2g}) hybridization, although a certain weak hybridization of this type still remains. Hence, conditions for the appearance of covalency of (sp, t_{2g}) type are not fulfilled.

b) Correct understanding of the above gap follows from the special geometry of the Brillouin zone (BZ) of the simple cubic* (SC) and BCC lattices[13]. Namely, point M (endpoint of the direction Σ on the boundary of the first as well as the 2nd (dodecahedral) BZ of the SC lattice) from the neighbourhood of which this gap is derived, coincides with the point N (also endpoint of the Σ direction) on the

TABLE IV

Partial wave analysis for two energy branches delimiting the NHG in Σ_4 states (*cf.* also Table VIII or ref.[4], especially the reversed order of M_5· and M_2 energy levels)

Point:	Γ	Σ (middle)	M
IR	15	4	5'
E(Ry)	1·0645	0·7046	0·4717
C(Cu) %	26·899p	20·923p	24·777p
		12·455e_g	
C(Zn) %	42·145p	31·911p	36·617p
		3·977e_g	
IR	12	4	2
E(Ry)	0·2977	0·3167	0·3785
C(Cu) %	91·337e_g	87·087e_g	99·077e_g
		1·802p	
C(Zn) %	2·672e_g	2·339p	—
		1·515e_g	

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*   Simple cubic BZ is the appropriate Brillouin zone for the B2 lattice as well as for the L1$_2$ lattice of the ordered Cu$_3$Au considered below.

boundary of the 1st BZ of the disordered β-CuZn BCC lattice. As typical high symmetry points of BZ boundaries, the points M and N are connected with the existence of gaps in the band structure of the respective crystal phases. The key property here is that the gap of M and the gap of N are as a matter of fact identical and hence the same for both the ordered β'(B2) as well as the disordered β(BCC) phase. As to the character of this gap, it is difficult to prove whether it is a HG or NHG in sp states, for reasons mentioned above.

In connection with superstructure effects to be discussed below, it is important to notice that the concept of folding[4,5] of energy bands from BCC into the SC BZ is of no use here. An interaction between Σ and G energy branches is switched on by folding at the point N. Howerer, no gap opens due to this mechanism at E_F for CuZn. Also at X', the midpoint of the direction Δ of the BCC BZ, where such a folding occurs, there is no gap in the B2 lattice band structure at E_F (although such a gap exists at lower energies, compare *e.g.* Fig. 9 in ref.[12]).

 c) At E_F, there is no gap (NHG) that would separate pure $d(e_g)$- from pure sp-bands. This was the case with aluminides, where especially the pronounced peak in the d-state density at E_F was mainly responsible for a rather pronounced ionicity[3].

TABLE V

Partial wave analysis for two energy branches delimiting the HG in Λ_3 states (*cf.* also Table XI of ref.[4])

Point:	Γ	Λ (middle)	R
IR	25'	3	12
E(Ry)	0·3633	0·3398	0·3792
C(Cu) %	97·791t_{2g}	95·278d^a	99·196e_g
		0·114p	
C(Zn) %	0·950t_{2g}	1·066d	—
		0·322p	
IR	12	3	25'
E(Ry)	0·2977	0·3141	0·2664
C(Cu) %	91·337e_g	87·703d	82·566t_{2g}
		1·189p	
C(Zn) %	2·672e_g	3·514p	8·913p
		1·264d	

^{a} $d = e_g + t_{2g}$.

With β′-CuZn, the separation in energy of d- and sp-bands is large and the former lie deep below E_F.

d) Although effective charges δ_e on the atoms do not follow from our partial wave analysis, they have been calculated in ref.[11,13] and show a weak ionicity of β′-CuZn ($\delta_e \approx 0.08e$, the copper atoms being negatively charged).

e) In principle, this weak ionicity can stem from both types of hybridization mixing, (s, p) and (sp, t_{2g}), since according to *b*), there is a little probability that the very weak sp covalency, even if present, would compensate for charge transfer in sp-states.

Naturally, the question remains to be answered, why effective charges of β′-CuZn are small but still finite. One can argue in two ways. First, since these charges are the result of a self-consistent procedure, they are determined[3,14] by the amount of charge that can flow through E_F during the change of the crystal potential. Due to the very small value $n(E_F)$ of the density of states at E_F in the upper dip, an unrealistically large change in the potential would be required to carry out a considerable charge transfer. Hence, such a situation does not occur. Second, in an alloy like CuZn with mainly metallic electrons, the charge tends to be evenly distributed throughout the system. Without screening, the effective charges on Zn and Cu atoms would be equal[15] to ± 0.5 e, respectively. Complete screening would rule them out. However, since the density of free carriers at E_F is low due to the existence of the upper dip in $n(E)$, the screening is not complete and a small amount of charge survives on the atoms[15].

Let us describe the picture of the development of the ordered β′ phase in the CuZn alloy as accepted in the literature[12,13,16] and as follows from the present work. The energy band structure in the region of the upper dip is to a large extent characterized by free-electron like sp-bands. The form of the Fermi surface (FS) and especially its contact with the BZ boundaries of the various crystal phases in question is of main importance here (see Hume–Rothery rules as interpreted by Jones[16]). At low temperatures and low concentration of zinc, the α(FCC) phase is stable. When the zinc concentration increases, FS approaches the boundary of the 2nd SC BZ and hence, the β′(B2) phase gets stabilized. For a certain range of concentrations, it coexists with the original α phase. Close to and at the moment of contact of FS with this BZ, one has a pure β′ phase. When further zinc is added, the new γ phase appears. Naturally, same argumentation could be also applied to the high-temperature β(BCC) phase as follows from the discussion of item *b*) above and the fact that the 2nd (dodecahedral) SC BZ coincides with the 1st BZ of the BCC lattice. However, at low temperatures, nature apparently prefers the β′-phase since by allowing for charge transfer and ionic lattice ordering, energy is lowered. In the disordered phase, ionicity is largely suppressed. Namely, for each Cu (or Zn) atom, there is always a certain probability to be partly surrounded by the atoms of the

same kind. The existence of effective charges (arising due to the difference in atomic electronegativities), would then contradict the concept of electronegativity itself.

The elucidation of the somewhat exceptional position of the ordered β'-brass among the other investigated phases of binary alloys was the main interest of the present paper. Although possible phase transitions from the disordered (α, β) to the ordered (β') phase are undoubtedly caused by the change in the character of bonding (the appearance of ionicity), reliable information on electronic specific heat or susceptibility or a theoretical calculation which would show the relevant behaviour of $n(E_F)$, seem to be still missing.

It is interesting to notice that a free-electron like system exists which is in some respect analogous to the CuZn alloy, namely the alloy of Cu and Au. At low Au concentrations, it also exhibits a disordered α(FCC) phase. Same reasoning about FS and BZ as given for CuZn ordering can be applied here[17] (see the touching of the Cu_3Au FS to the 2nd (dodecahedral) SC BZ at Au partial fraction equal to one fourth) with the exception, that a BCC disordered phase is geometrically and energetically improbable here since both copper and gold are FCC metals. Hence, with Cu_3Au, the ordered state is automatically the $L1_2$ structure (four interpenetrating SC lattices) without the necessity of invoking charge transfer, as was the case for β'-CuZn. Main difference between the above two systems consists in the fact that with Cu_3Au one deals with a real superstructure effect[17–19] which develops when going from the disordered FCC into the ordered phase. Contrary to β'-CuZn, where the ordered phase is not a superstructure of the FCC phase, folding of FCC energy bands into the SC BZ brings[18] an important physical consequence here. Namely, for the Σ branch folded around the M point, a new gap opens at E_F as can be seen from the $L1_2$ energy band structure[19,20]. Folding around X' again does not bring anything new. (Notice, however, that except for a change in the energy scale, there is a similarity between the band structures[6,19] of β'-CuZn and ordered Cu_3Au for the important Σ and Z branches around the point M at E_F.)

Measurements on the de Haas-van Alfen effect[17] and positron annihilation[21] justify the above picture for β'-CuZn as well as for ordered Cu_3Au. They show the existence of a gap in β'-CuZn near M that lies at E_F (see ref.[21]) and detect clearly the analogous gap in ordered Cu_3Au arising due to the superstructure effect (see Fig. 1a in ref.[17]). Besides that, both in Cu_3Au (see Fig. 1b of ref.[17]) and α-CuZn (Figs 1 and 2 in ref.[22]) they show a gap around R (endpoint of the (111) direction lying on the boundary of the FCC BZ), located at E_F. Recent photoelectron spectroscopy measurements[23] discovered Shockley surface states on the (111) face of ordered Cu_3Au which apparently stem from this gap. As with the Cu(111) surface, this gap must be a HG. Similar search for Shockley surface states on the (111) face of α (but not β or β'!)-CuZn seems very promising, particularly because these as well as Tamm surface states are well known with α-CuAl, where they exist for other crystal faces as well[24].

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