PROJECTED SURFACE ENERGY BANDS, SHOCKLEY SURFACE STATES AND STABILITY OF ORDERED SUBSTITUTIONAL ALLOYS WITH CsCl STRUCTURE: THE EXAMPLE OF β'-CuZn

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Qualitative theory of Shockley surface states is applied to β'-CuZn with the aim to analyse the character and location of its hybridizational gaps and to draw general conclusions on other ordered substitutional alloys with CsCl structure as well. The results are used to propose the role which hybridizational gaps and chemical bonding can play in order-disorder phenomena of such alloys. Some special questions of relevance to these phenomena are also qualitatively discussed.

Recently, the authors performed an analysis of the existence of Shockley surface states (SS) and bonding for two representatives of transition metal monocompounds with rock-salt structure, titanium[1] and niobium[2,3] carbides, using qualitative theory[4-6]. The results allowed conclusions on nitrides and oxides of transition metals as well. It appeared that the frequency of the occurrence of SS was much smaller as compared with pure transition metals.

In the present paper, we have undertaken the same analysis for a typical ordered substitutional alloy (OA) with simple cubic (CsCl) structure, β'-CuZn (ref.[7,8]). It turns out that here, SS should occur as frequently as with the original noble metal Cu (ref.[6]). To understand this, let us dwell shortly on a simple description of the electronic structure of β'-CuZn.

The introduction of Zn atoms into the Cu metal brings about the following situation close to the Fermi energy E_F. With the exception of the 4*p*-like band of copper and the 3*d*-like band of zinc, all other valence electron bands[8] participate in pronounced hybridizations near E_F. The Zn 3*d*-like band does not intervene since it lies at lower energies and the Cu 4*p*-like band is pushed away to higher energies by the interaction with Zn 4*s*,4*p* electrons. Therefore, due to the strong overlap between s, d bands of Cu and s, p bands of Zn, hybridization gaps (HG) and SS of (s, d) and (p, d) type are to be expected here (for the definition of a HG see the next section). The largest contribution to the s or p character comes from Zn atoms whereas for the d character Cu atoms are exclusively responsible. The contribution of copper to the s character can sometimes be compared with that of zinc[8]. Apart from (s, d) and (p, d) HG, one finds also HG of (d, d) character. The rare occurrence of HG and SS

with transition metal monocompounds follows from the fact, that in that case, overlap occurs only between bands of p states of non-metal atoms and of t_{2g} states of metal atoms and even this in fact only with carbides. With nitrides and oxides such an overlap does not exist which results in the absence of (p, t_{2g}) HG. As a consequence, the bonding in these compounds has a decreasing covalency component and the ionic character of bonding and the effective charges on the constituent atoms increase when one moves from carbides to nitrides and oxides. Examples of a similar violation of local charge neutrality with OA also exist and are discussed in the present paper.

As to the model of the crystal surface (Shockley model)[4,9], an ideal termination of the crystal is treated here only. Besides of general problems[4,5] connected with such an approximation, the surface segregation problem arises with OA. This complication can become more or less serious depending on the experimental conditions of surface preparation[10], as well as on the crystal face investigated. For β'-CuZn, the ideal (001) and (111) faces are monoatomic, containing only one type of atoms. The (011) face is heteroatomic. As a rule, the surface enriches in the component with lower surface energy (higher volatility) so that Zn surfaces should be less affected by segregation Unfortunately, for OA such effects have not yet been fully studied theoretically, only some partial results exist[11].

For β'-CuZn, the data on volume state energies used in the present paper are given in[7]. In the symmetry analysis, results of[8] have also been utilized and a Cu atom has been located at the origin of coordinates. Notice, that this choice is not consistent with[7]. For certain values of $\boldsymbol{k}_{\parallel}$, the analysis of symmetry properties of wavefunctions depends on the origin of coordinates (Cu or Zn). It would be interesting whether polarized light angle-resolved photoelectron emission[12] could distinguish between Cu and Zn orbitals.

Apart from the analysis of SS, relation between SS, chemical bonding and OA stability is of primary interest here. For alloy phases, five criteria of stability are known from the literature[13]: geometrical structure, atomic size, electronegativity, electronic concentration per atom (Hume–Rothery rules) and chemical bonding. The last three are mentioned here, main emphasis concentrates on the last one. Our point of view is explained in sections General Rules and Discussion. The former section contains also a short description of the use of general rules of SS existence (GR) for substitutional alloys, both ordered and disordered. Results of the application of the qualitative analysis to β'-CuZn are presented. Some physically interesting consequences are shortly discussed including chemisorption and catalysis and β'-CuZn is compared with other β'-brass type alloys. The Appendix gives the correspondence between the 3-dim Brillouin zone of the simple cubic lattice and the surface Brillouin zones (SBZ) of the three crystal faces investigated.

GENERAL RULES OF SS EXISTENCE, BONDING AND STABILITY

Qualitative theory of SS enables to analyse SS and chemical bonding in solids. Two important questions can be answered by this theory: *1*) Whether the surface of a particular solid can exhibit SS (dangling bonds), *2*) Which kind of bonding is responsible for their appearance in this solid. The theory depends critically on symmetry considerations, and sufficiently detailed information on symmetry properties are indispensable for its application. Nevertheless, it is possible to use it even for alloys preserving at least a certain kind of symmetry. Substitutional alloys (where the regular lattice is randomly occupied by atoms constituting the alloy) can serve as an example.

The theory consists of two ingredients: *a*) projected surface energy bands (SP) and *b*) general rules of SS existence (GR). For a particular value of $\boldsymbol{k}_{\parallel}$ in SBZ, SP help to find gaps in the energy spectrum of a finite crystal* with an arbitrary surface. In fact, SP represent the projection of the bulk band structure with respect to a (low index) plane plotted as a function of $\boldsymbol{k}_{\parallel}$. The information on SS and chemical bonding, connected with a gap, is contained in GR. These are summarized in three rules[5,14]: GR *1*) Any gap is either hybridizational (HG) or nonhybridizational (NHG); GR *2*) SS can exist in HG only; GR *3*) In a solid a HG can contain one or two SS for a point in SBZ where this HG exists. Which of these two alternatives takes place in a particular case is decided by the number of "hybrid orbitals" per surface elementary cell cut in the process of surface formation.

The gap is a HG if, with hybridization neglected, two bands of volume states cross, *i.e.* if in the HG formation the respective two dispersion curves $E^0(\boldsymbol{k})$, each of definite character (*e.g. s*, *p* or *d*), play a dominant dole. These curves derive from mutually non-interacting Bloch functions based on different types of orbitals (*s*, *p* or *d*) located on the same or different types of atoms (Cu or Zn in our case). By switching on Bloch function mixing, a HG appears. From this point on, one can also speak of a "hybrid orbital"[14] as originating from the hybridization of orbitals that gives rise to the particular HG. The whole effect is most easily interpreted *e.g.* in the LCAO or KKR (scattered wave) pictures. For a more formal interpretation, the concept of the complex band structure[15] can be used. Sometimes the term strong hybridization is used in this situation and it is understood that all other cases lead to weak (or no) hybridization[16]. The gaps which are not HG are NHG by definition. Any gap can be either a real or a resonance gap. A resonance gap lies in states of one symmetry, being at the same time immersed in states of different symmetry. Interesting gaps are the so-called double gaps of crossing type which consist of two parts, one hybridizational and the other usually non-hybridizational[5,6]. GR remain valid for disordered systems mentioned above[14]. Naturally, some of the dispersion curves of volume states can have finite width[17]. The more important change is, however,

* By finite we mean either very large finite or semiinfinite specimens.

that the symmetry of the system increases suddenly during the order-disorder transition. With OA (which are heteroatomic systems), most interesting gaps arise from the interaction of (neighbouring) heteroatoms. In such gaps, a new type of surface states can also exist which has been described e.g. on p. 256 of[9]. Such surface states can exist also with disordered alloys.

For the very high symmetry points of SBZ of a given crystal surface, the type and the number of "hybrid orbitals" is determined solely by symmetry considerations. The symmetry reasoning gives basis functions in the elementary cell of any crystal layer. These functions transform according to a certain irreducible representation of the symmetry group of such a high-symmetry point. When a HG appears in the states of this irreducible representation, "hybrid orbitals" are formed from those basis functions which are responsible for the formation of this HG. The number of "hybrid orbitals" is controlled by the dimensions and number of different irreducible representations for which the HG is a common gap. For the existence of a SS, it is crucial that its "hybrid orbital" is cut by the surface formation. As an example, let us consider two different (p, d) HG which incidentally almost coincide, one in $\bar{S}_{1,4}$ and the other in $\bar{S}_{2,3}$ states on the (011) face of β'-CuZn (Fig. 3). For the surface layer, the p- and d-type basis functions of the one-dimensional representations $\bar{S}_1$ and $\bar{S}_4$ are given by $[yz, 3x^2 - r^2, y - z]$ and $[y^2 - z^2, y + z]$. For representations $\bar{S}_2$ and $\bar{S}_3$ they are $[x(y - z), x]$ and $x(y + z)$. In this particular case, a special situation takes place where the lattice can be looked upon as composed of two types of layers, even and odd. When going from an even to an odd layer, it is necessary to interchange $\bar{S}_1$ and $\bar{S}_4$ basis functions, and similarly $\bar{S}_2 \leftrightarrow \bar{S}_3$ holds. Here, hybridization mixes Bloch functions of the two neighbouring layers.

The important point is, that qualitative theory relates strong hybridization with the chemical term covalency. Therefore, when strong hybridization is found, the bonding of the solid can contain a covalent component. The importance of this component in a particular solid depends *a*) on the extent of the respective HG in $\boldsymbol{k}$-space, *b*) on the degree to which states that are bonding (antibonding) with respect to this HG are occupied (empty). These factors decide, for example, that covalency decreases in the sequence diamond → VI B transition metals (*e.g.* Mo) → polyvalent metals like Al (here one usually does not speak about covalency, and the whole effect is clearly only marginal), although HG and SS can naturally be found in each of these systems. Hence, strong hybridization is a necessary condition for covalency which, under the above conditions, triggers the development of the covalent component of bonding in a particular system. In qualitative theory, however, strong hybridization is defined to be equivalent to the generalized notion of "bond". Such a "bond" is more general as compared with its classical chemical meaning which corresponds to situations where a HG exists for the whole Brillouin zone (*e.g.* Si). The generalization includes also systems sometimes called electron deficient, in which there are less electrons per atom available than neighbouring atoms to bind. Consequently, the "bond"

bears to a certain degree a resonant (mesomeric) character. The surface plane can be thought of as an imaginary plane in the bulk which cuts all interactions. Those which bear some covalent character can be detected by the direct use of GR.

For systems studied in the present paper, GR can also help to clarify the relation between bonding and stability[14]. As we shall see in the Discussion, the transition from the disordered to the ordered phase is accompanied by the opening of some HG (or NHG, naturally main emphasis here will be on HG) causing the appearance of dips in the density of states of the ordered phase. If the Fermi energy falls in such a dip, total electronic energy is lowered during the ordering process and the whole effect[18–22] can be considered as a triggering mechanism for the transition. This is supported by the fact that the entropic contribution to the free energy is small. Its electronic part[23,24] is small due to the dip in the density of states at E_F and its vibrational part due to the covalent component of bonding caused by the particular HG. In terms of "bonds", the stabilization mechanism can be paraphrased as follows. A "bond" originating from a HG stabilizes the ordered phase depending on the occupation numbers n_b and n_a of the respective bonding and antibonding energy levels. The number n of "bonds" per surface elementary cell, cut by the above mentioned imaginary plane, which are really effective in the stabilization, can be estimated from[25]

$$n \cong (1/N) \cdot \tfrac{1}{2} \sum_{\boldsymbol{k}_\parallel} [n_b(\boldsymbol{k}_\parallel) - n_a(\boldsymbol{k}_\parallel)] ,$$

where N is the number of surface elementary cells (the number of $\boldsymbol{k}_\parallel$ points in the surface Brillouin zone) and the summation extends over all occupied states with $\boldsymbol{k}_\parallel$ where the respective hybridization takes place. As expected, n reaches its maximum for E_F lying inside the HG.

A certain overlap with the above ideas on chemical bonding in metals and alloys and phase (especially superstructure) stability can be traced *e.g.* in[26–29] as well as[18–20,24].

RESULTS

The (001) *Face*

First, let us consider the $\bar{\Delta}$ and $\bar{\Sigma}$ directions of the surface Brillouin zone (Fig. 1 and Table I). In the point $\bar{\Gamma}$, HG exist in $\bar{\Gamma}_1$ states only. The lower HG is of (s, e_g) character* where the *s*-component contains contribution from the Zn as well as the Cu atoms. It is a double gap which, not far from $\bar{\Gamma}$, changes into NHG in both $\bar{\Delta}$ and $\bar{\Sigma}$ directions. Along $\bar{\Delta}(\bar{\Sigma})$, the crossing is due to $Z_{1,3}(S_{1,3})$ branches of volume

* Note that here, contrary to transition metal monocompounds, the relation $E(\Gamma_{12}) < E(\Gamma_{25'})$ holds.

states. Next is a (p, e_g) HG in $\bar{\Gamma}_1$, which is separated into a couple of HG when one moves from $\bar{\Gamma}$. For $\bar{\Delta}$, the lower one seems to have (t_{2g}, e_g) hybridization, whereas the upper has probably (p, d) hybridization. For $\bar{\Sigma}$, the lower gap is a double gap in $\bar{\Sigma}_1$ states. In $\bar{\Sigma}_2$ states, the gap is also a double gap consisting from three parts, the middle one being a (e_g, t_{2g}) HG. The remaining gaps along $\bar{\Delta}$ and $\bar{\Sigma}$ directions are NHG with the exception of an important wide (p, d) HG around E_F in $\bar{\Delta}_1$ states. At $\bar{X}$, this gap exists in both $\bar{X}_1$ and $\bar{X}_3$ states and along the $\bar{Z}$ direction it extends in $\bar{Z}_1$ as well as in $\bar{Z}_2$ states. Its (p, d) character at $\bar{X}$ clearly follows from the definition since along the $(M_{5'}-Z_1-X_1)$ and $(M_{5'}-Z_3-X_5)$ branches which project on $\bar{X}_1$ and $\bar{X}_3$, the character of the Bloch function changes from p (mainly Zn) at M to d (Cu) at X. The Bloch functions of the $Z_{1,3}$ branches above E_F are also appropriately hybridized (see Fig. 2 and Table II of ref.[8]). This HG exists almost for the whole surface Brillouin zone. In the point $\bar{X}$, an additional HG of (s, t_{2g}) character can be found in $\bar{X}_3$ states at lower energies. It survives also in $\bar{Z}_2$ states. Two lowest gaps in $\bar{Z}_1$ states are of (p, d) character with strong s(Cu) component for the lower gap and of (t_{2g}, e_g) character for the upper one. Other gaps along $\bar{Z}$ are NHG.

Existence conditions of the most important HG are shown in Figs 1, 2.

The (011) Face

We shall begin with the $\bar{\Sigma}$ direction. In $\bar{\Sigma}_1$ states, the lowest gap is a (s, d) HG. This gap extends also along the whole $\bar{\Delta}$ and $\bar{C}$ and a part of $\bar{D}$ directions (Figs 3, 4). It exhibits two double gap crossings (Fig. 3) and in the part of $\bar{\Delta}$ direction joining $\bar{\Gamma}$

TABLE I

HG on (001) Face of β'-CuZn Summarized by Giving Typical Energy (E), Character of Each Particular HG and Location on Fig. 1

E, Ryd	Character of HG	Location on Fig. 1
0·17	$(s, e_g)^a$	$\bar{\Gamma}_1, \bar{\Delta}_1, \bar{\Sigma}_1$
0·25	$(s + p, t_{2g})$	$\bar{Z}_2$
0·3	$(t_{2g}, e_g)^a$	$\bar{\Sigma}_2$
0·3	(t_{2g}, e_g)	$\bar{\Delta}_1, \bar{\Sigma}_1{}^a, \bar{Z}_1$
0·35	(p, d)	$\bar{Z}_1$
0·35	(p, e_g)	$\bar{\Gamma}_1$
0·4	(p, d)	$\bar{\Delta}_1, \bar{\Sigma}_1$
0·6	(p, d)	$\bar{\Delta}_1, \bar{Z}_{1,2}, \bar{X}_{1,3}$

[a] Double gap (DG).

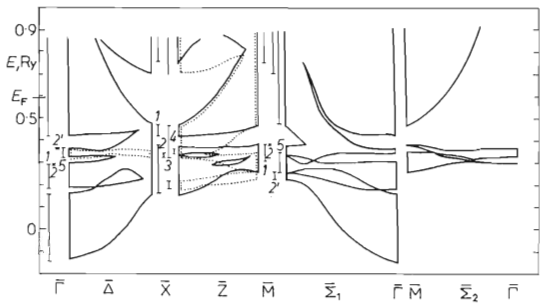

FIG. 1

Projected Surface Energy Bands of (001) Face of β'-CuZn

Along $\bar{\Delta}$ and $\bar{Z}$, area within full lines corresponds to symmetrical representation of symmetry group C_s, area within dotted lines to antisymmetrical one. States corresponding to various irreducible representations in high symmetry points $\bar{\Gamma}$, $\bar{X}$, $\bar{M}$ are also shown.

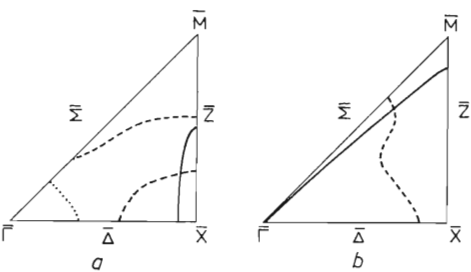

FIG. 2

Existence Conditions for Hybridizational Gaps (HG) of (001) Face in the Irreducible Part of Surface Brillouin Zone

a The lowest (s, e_g) DG (area within full line adjacent to $\bar{\Gamma}$, double gap crossing marked by dotts), and (t_{2g}, e_g) HG (area within dashed lines adjacent to $\bar{\Gamma}$); *b* the lower (p, d) HG (area within dashed line adjacent to $\bar{\Gamma}$), and the upper (p, d) HG (area within full line adjacent to $\bar{X}$).

it shows the same hybridization as along $\bar{\Sigma}$. At $\bar{\Gamma}$, it is the lower of the two gaps in $\bar{\Gamma}_1$ which arise from the hybridization of three non-interacting branches $\Gamma_1 - \Sigma_1 - M_5$, $(s + p)$, $\bar{\Gamma}_{25'} - \Sigma_1 - M_3$ (t_{2g}) and $\Gamma_{12} - \Sigma_1 - M_1$ (e_g). The second gap from below in $\bar{\Sigma}_1$ states is a double gap formed by the crossing of T_1 and T_5 branches of volume states. It is a (t_{2g}, e_g) HG on the right from the crossing. Next is the important (p, d) HG around E_F which, contrary to the (001) face, is a resonance gap in $\bar{\Sigma}_1$. The lower of two gaps in $\bar{\Sigma}_2$ states is a (t_{2g}, e_g) HG as follows *e.g.* from the hybridization of two non-interacting branches $\Gamma_{12} - \Lambda_3 - R_{12}(e_g)$ and $\Gamma_{25'} - \Lambda_3 - R_{25'}$ (t_{2g}) of volume states.

From the remaining HG below E_F only one is more pronounced, namely that of (p, d) character around 0·4 Ryd in $\bar{D}_1$ and a part of $\bar{C}_{1,2}$ states near $\bar{S}$. The rest can be found in Table II, which is not quite complete due to the lack of symmetry information. Above and around E_F, the broad prominent HG already discussed with the (001) face, extends as a (p, d) HG all along the Fig. 3 (see Fig. 4 for the existence condition). In the middle of $\bar{C}$, it appears as a double gap with the interesting property of being hybridizational on both sides of the crossing. For these two sides, however, the HG have different properties. Near $\bar{S}$, the HG should contain altogether four SS. This happens because this gap is a superposition of two HG as can be seen from SP along $\bar{\Delta}$ in Fig. 3 (see section General Rules). Near $\bar{Y}$, only two SS should be found according to GR 3. Similar situation has been found[6] with the (s, p) HG on the (001) face of Cu.

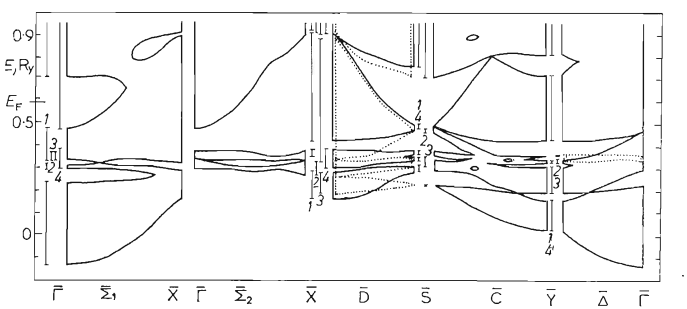

FIG. 3

Projected Surface Energy Bands of (011) Face of β'-CuZn
Cf. text to Fig. 1.

The (111) Face

At the $\bar{\Gamma}$ point of the surface Brillouin zone, we find a (s, t_{2g}) HG (Fig. 5, Table III) in $\bar{\Gamma}_1(\Lambda_1)$states and a (e_g, t_{2g}) HG in $\bar{\Gamma}_3(\Lambda_3)$ states (the lower gap), both lying below E_F. Properties of SS in the $\bar{\Gamma}_3$ HG are discussed in more detail further. The lowest gaps in $\bar{T}$, $\bar{T}'$ and $\bar{\Sigma}(\bar{\Sigma}_1)$ directions are HG of (s, d) type. Moreover, the $\bar{\Gamma}_3$ HG extends along a part of $\bar{T}$ and $\bar{\Sigma}$ directions, in the latter case for both $\bar{\Sigma}_1$ and $\bar{\Sigma}_2$ states. Let us mention that both $\bar{\Sigma}_1$ and $\bar{\Sigma}_2$ gaps are double gaps arising due to T_1, T_5 and Σ_2, Σ_4 crossings, respectively, (see Fig. 2 of[8]) with the HG part near $\bar{\Gamma}$. Finally, there is a wide (p, d) HG in the vicinity of the $\bar{K}$ point, placed just above E_F. The character of several remaining narrow gaps near $\bar{K}$ is difficult to decide.

DISCUSSION

The analysis of the last section, summarized in Tables I–III, shows that many HG appear with β'-CuZn. A part of these HG, however, are very narrow and not suitable for direct experimental verification of the existence of SS. For this purpose, SS of the more pronounced HG of (s, d) and (p, d) type are of interest. The (s, d) HG lie below E_F and the respective SS should therefore be seen by means of the angle-resolved photoemission spectroscopy, whereas those from (p, d) HG lying both below and around E_F could be studied also by electron energy-loss spectroscopy. Up to now, the few existing experiments on alloys[10,30,31] concentrated mainly on global features of the electronic structure, *e.g.* on the detection of virtual bound

TABLE II

HG on (011) Face of β'-CuZn as Presented on Fig. 3

E, Ryd	Character of HG	Location on Fig. 3
0·25	(s, d)	$\bar{\Gamma}_1$, $\bar{\Delta}_1$, $\bar{C}_{1,2}$, $\bar{D}_{1,2}$, $\bar{\Sigma}_1$
0·3	(t_{2g}, e_g)	$\bar{\Sigma}_1{}^a$, $\bar{X}_3$, $\bar{D}_1$, $\bar{S}_{1,4}$
0·32	(t_{2g}, e_g)	$\bar{\Sigma}_2$
0·4	(p, d)	$\bar{D}_1$, $\bar{C}_{1,2}$, $\bar{S}_{1,4}$
0·6	(p, d)	$\bar{\Gamma}_1$, $\bar{\Delta}_1$, $\bar{\Sigma}_1$, $\bar{S}$, $\bar{D}_{1,2}$, $\bar{C}_{1,4}$, $\bar{Y}_{1,4}$

[a] Double gap.

states[30] *etc.* Although the mechanism of the virtual bound state formation is also hybridizational as that of a SS, ref.[32], much finer resolution and better experimentally defined alloy surfaces are needed to study SS.

The qualitative approach enables not only to make statements about the occurrence and energy of SS, but also about the symmetry of their wave functions. An interesting situation occurs with the $\bar{\Gamma}_3(e_g, t_{2g})$ HG on the (111) face of β'-CuZn. The respective SS are doubly degenerate and each of the two SS wave functions exposes two lobes with opposite sign to the vacuum. This behaviour is the first condition of a simple theory of chemisorption and catalysis[33] based on Woodward–Hoffmann rules[34]. The second condition requires that the SS energy lies near E_F. Naturally, this is not fulfilled for β'-CuZn itself but for some other β'-brass type alloys with less valence electrons per unit cell, *e.g.* FeAl (ref.[20,35,36]). The same theory has already been used in the case of NbC (ref.[2,3]) and TiC (ref.[1]) where (p, t_{2g}) SS intervene.

TABLE III
HG on (111) Face of β'-CuZn as Presented on Fig. 5

E, Ryd	Character of HG	Location on Fig. 5
0·25	(s, d)	$\bar{\Gamma}, \bar{\Gamma}', \bar{\Sigma}_1$
0·3	(s, t_{2g})	$\bar{\Gamma}_1$
0·32	(e_g, t_{2g})	$\bar{\Gamma}_3, \bar{\Gamma}, \bar{\Sigma}_{1,2}$[a]
0·7	(p, d)	$\bar{\Gamma}, \bar{\Gamma}', \bar{\Sigma}_1$

[a] Double gap.

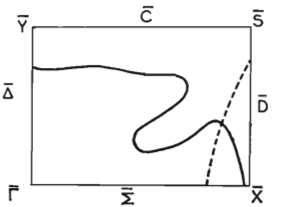

FIG. 4
Existence Conditions for Two Most Prominent HG of (011) Face in Irreducible Part of Surface Brillouin Zone

For lower double gap (area within dashed line adjacent to $\bar{\Gamma}$) with (s, d) HG part near $\bar{\Gamma}$, and upper (p, d) HG (area within full line adjacent to $\bar{S}$).

As seen from Figs 1–5, the most pronounced HG on the three faces of β'-CuZn investigated in the present paper, are the two (p, d) HG of which the lower lies below E_F and the higher is situated in the same energy region as E_F (E_F falls into this gap). Both these HG have rather extended existence conditions (Figs. 2, 4). In the electronic density of states[7,8,37] they give rise to two well separated and pronounced dips. This behaviour is typical of ordered β'-brass type alloys[20,35–38] where one atom of the unit cell is a transition or noble metal (d-metal) and the other a non-transition (sp) metal. As discussed earlier, this can be very important for the interpretation of the stability of ordered (β') phases since in the respective disordered (β) case, the dips in the density of states are expected to disappear.

In support of the relation between phase stability and HG one can mention that β'-brass type alloys are split into two subgroups according to where the E_F falls. With the first subgroup, comprising, *e.g.* CuZn (ref.[7,8,37]), NiAl (ref.[35,37–40]), AuZn (ref.[39,40]), AgMg (ref.[41]) and CuBe (ref. [37]), E_F falls into the higher HG. For these alloys, our interpretation of the ordered phase stability is essentially equivalent to Hume–Rothery rules. In this case *1*) the alloy Fermi surface is not too far from free-electron like[40], *2*) the situation around E_F can be interpreted as due to the contact of this Fermi surface with the faces of the second (dodecahedral) Brillouin zone of volume states near point M (ref.[40]) (see points $\bar{\Gamma}$ of the (011) face and $\bar{X}$ of the (001) face of Figs 1, 3 of the present paper), *3*) at least with NiAl, the zero valence of Ni (*i.e.* the $d^{10}s^0$ configuration) postulated by Hume–Rothery

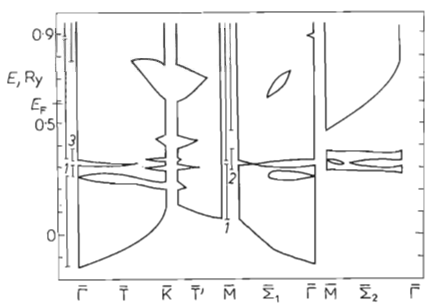

FIG. 5
Projected Surface Energy Bands of (111) Face of β'-CuZn
Cf. text to Fig. 1.

theory can be justified. This follows from band structure calculations[20,35,37–39] and X-ray photoemission experiments[31] which find the nickel *d*-band fully occupied. Also, a comparatively small Al → Ni charge transfer has been found theoretically[37].

With the second subgroup which includes, *e.g.* FeAl (ref.[20,36]), CoAl, CoBe and NiZn (ref.[37]), E_F falls into the lower HG. Although Hume–Rothery rules can be formally applied also to FeAl and CoAl, they cannot be justified by band structure calculations, since Fermi surfaces of the compounds of this subgroup are far from free-electron like. The lower HG occurs at different Brillouin zone points (*e.g.* at X) and the "zero valency" of Fe and Co presents also serious problems.

Interesting enough, the two OA subgroups largely differ in their stability with respect to the temperature. Members of the second subgroup either display much higher transition temperatures or are stable up to their (very high) melting points[42,43].

Let us analyse from the present point of view the stability of other OA with CsCl structure. Formally, they differ in metal atoms (*d* or *sp*) from which they are constituted. The first group, the *sp*–*d* type alloys, has just been treated. The second group consists of *d*–*d* alloys in which both atoms are transition metals. In the last group *sp*–*sp* systems are found. This classification reflects some differences in the stabilization mechanism of the ordered phase. They will now be briefly illustrated.

First, let us start with *d*–*d* alloys. TiFe (ref.[44]) and FeCo (ref.[45]) will serve as examples. Since in this case, the electronic structure of both composing atoms is similar, energy bands of these alloys can be looked upon as those of a bcc transition metal on which a superstructure effect has been imposed. This effect causes the appearance of some additional gaps in SP of the bcc case[5,45]. Such changes have already been discussed[5] for antiferromagnetic superstructure of chromium[46]. For the alloy lattice, the additional features are: *a*) One HG on the (011) face at $\bar{\Gamma}$ arising from (t_{2g}, t_{2g}) hybridization of Σ_3 and G_3 branches of volume states (Fig. 2*c* of ref.[45]), *b*) Two HG at $\bar{\Gamma}$ of the (111) face. The first is of (t_{2g}, t_{2g}) character and is due to the crossing of Λ_1 and F_1 branches on Fig. 2*b* of[45]. The second is (t_{2g}, e_g) type and originates from the crossing of the lower Λ_3 and F_3 branches in Fig. 2*b* of[45]. *c*) Several NHG at $\bar{\Gamma}$ of the (001) face resulting from the superstructure splitting of Δ states (Fig. 2*a* of ref.[45]).

In fact, TiFe and CoFe are representants of two subgroups of *d*–*d* OA, which differ in stability and sharpness of the existence conditions of the ordered phase. The TiFe subgroup exhibits greater stability (higher temperatures of the order-disorder transition, narrower ranges of existence with respect to composition and more frequent occurence in nature). The FeCo subgroup shows an opposite behaviour. This is natural, since the stability of the ordered phase is large when atoms A and B lie on different sides of Cr in the periodic table and together have same number of valence electrons per atom as chromium[47]. In this case again (see section General Rules), the Fermi level of the alloy falls into the dip in the density of states[19,44]

caused by the ordered phase formation. Opposite to $sp-d$ OA, the dip arises due to both HG and NHG mentioned above. It appears, that for the stability of $d-d$ OA, two components of bonding are important: *a*) the covalent component related to the HG and *b*) the ionic component (charge transfer effects) closely connected with the NHG around E_F. This component is particularly clearly developped *e.g.* with ScCu (ref.[19,48]). Similarly to $sp-d$ OA, $d-d$ OA also exhibit a HG (and SS) interesting for chemisorption and catalysis. Again, it lies in $\bar{\Gamma}_3$ states on the (111) face, it has a (t_{2g}, e_g) character and is not due to the superstructure effect. Owing to the $\Lambda_1 - \Gamma_1$ splitting, it is a real gap (similar to antiferromagnetic Cr and unl ke *e.g.* Fe (ref.[49]) where it was a resonance HG).

The third group of $sp-sp$ OA where systems like Mg(Tl, Hg) (ref.[51]) and Au (Cs, Rb) (ref.[50]) belong, do not show strong hybridization (HG). Only weak hybridization of *sp* states on the two sublattices has been observed in some cases[51] which do not cause any pronounced dips in the density of states at E_F. Charge transfer between these sublattices is probably the reason of stability. The importance of charge transfer for the ordered phase stability is seen most apparently with Au(Cs, Rb) where it is so large that it leads to strong ionicity of the alkali – Au bonding and to a broad NHG near E_F (ref.[50,52]).

The question of charge transfer in OA is an important one and deserves special attention[21,52,53]. We have found previously with transition metal monocompounds[2] that charge transfer becomes more important for more electronegative non-metal atoms (N, O). Although both composing atoms are metals here, appreciable charge transfer can take place when the difference in their electronegativities is large and when the metallic or covalent components of bonding (screening or electron sharing) are not strong enough to compensate such trends. The most natural definition of electronegativity is that of Slater[54]. This electronegativity is equal to the negative value of the local (atomic) Fermi energy and corresponds to the Mulliken definition for an atom[55]. With such a definition, the charge will flow from the atom with smaller to that with larger electronegativity, as usual. Such charge transfers have been discussed recently in numerical calculations[19,37,44,56]. Violation of local charge neutrality with alloys[57] might seem surprising at first sight, nevertheless, it is a well documented fact. The resulting Madelung energy certainly plays an important role in the stability of at least some OA (ref.[19,40,44,47,55]).

Our basic proposal about a stabilizing gap near E_F is not limited to OA with CsCl structure only, but can be traced also with several examples exhibiting other geometries (Ni_3Mn (ref.[58,59]), Pt_3Sn (ref.[60]) *etc.*). This idea seems to be a microscopic realization of the broken symmetry concept and the Landau phenomenological theory[61]. Phenomenological statistical models based on pair interaction[62,63] are also related to it since formally, ordering energies can be considered as originating from pair interactions[18,22,29,53,64]. It would be interesting to speculate and ask whether symmetry breaking stabilizes the system only when it leads to a gap near E_F.

APPENDIX

Points in 3-dimensional k-space are given, which project on high symmetry points and directions of the surface Brillouin zone of typical faces of the simple cubic lattice. α is a parameter along the high symmetry direction in SBZ; points which differ only in γ project on the same point of SBZ. Only nonequivalent points, which are not connected by a symmetry transformation, are given.

The reciprocal 2-dimensional lattice vectors $\boldsymbol{b}_{1,2}$ are given, and the unit of length π/a is used, where a is the lattice constant. Furthermore, $0 \leqq \alpha, \gamma \leqq 1$ holds.

High symmetry directions (points) of the 3-dimensional Brillouin zone of the simple cubic lattice projecting on high symmetry directions (points) of the surface Brillouin zone are listed together with compatibility relations for irreducibile representations of the corresponding 3- and 2-dimensional symmetry groups. (The BSW notation[65] is employed.)

The (001) face

$\boldsymbol{b}_1 = (2, 0, 0)$, $\boldsymbol{b}_2 = (0, 2, 0)$

$\overline{\Gamma} = (0, 0, \gamma)$, $\overline{\mathrm{X}} = (1, 0, \gamma)$, $\overline{\mathrm{M}} = (1, 1, \gamma)$, $\overline{\Delta} = (\alpha, 0, \gamma)$,

$\overline{\mathrm{Z}} = (1, \alpha, \gamma)$, $\overline{\Sigma} = (\alpha, \alpha, \gamma)$

$\overline{\Gamma}_i$ i = 1, 2, 1′, 2′, 5	$\overline{\mathrm{X}}_i$ i = 1, 2, 3, 4	$\overline{\mathrm{M}}_i$ i = 1, 2, 1′, 2′, 5
Δ_i	Z_i	T_i

$\overline{\Delta}$ 1 2	$\overline{\mathrm{Z}}$ 1 2	$\overline{\Sigma}$ 1 2
Δ 1, 2, 5 1′, 2′, 5′	Z, S 1, 4 2, 3	Σ, S 1, 3 2, 4
Z 1, 3 2, 4	T 1, 2, 5 1′, 2′, 5	Λ 1, 3 2, 3
Σ 1, 4 2, 3		

The (011) face

$\boldsymbol{b}_1 = (2, 0, 0)$, $\boldsymbol{b}_2 = (0, 1, -1)$

$\overline{\Gamma} = (0, \gamma, \gamma)$, $\overline{\mathrm{Y}} = (0, \gamma + \frac{1}{2}, \gamma - \frac{1}{2})$, $\overline{\mathrm{X}} = (1, \gamma, \gamma)$, $\overline{\mathrm{S}} = (1, \gamma + \frac{1}{2}, \gamma - \frac{1}{2})$,

$\overline{\Delta} = (0, \gamma + \alpha/2, \gamma - \alpha/2)$, $\overline{\Sigma} = (\alpha, \gamma, \gamma)$, $\overline{\mathrm{D}} = (1, \gamma + \alpha/2, \gamma - \alpha/2)$,

$\overline{\mathrm{C}} = (\alpha, \gamma + \frac{1}{2}, \gamma - \frac{1}{2})$

$\overline{\Gamma}_i$ i = 1, 2, 3, 4	$\overline{\mathrm{X}}_i$ i = 1, 2, 3, 4	$\overline{\mathrm{C}}$ 1, 2
Σ_i	S_i	Z 1, 2, 3, 4

$\bar{Y}$	1, 4	2, 3	$\bar{S}$	1, 4	2, 3
Σ (middle)	1, 4	2, 3	S (middle)	1, 4	2, 3
X	1, 2, 3′, 4′, 5, 5′	3, 4, 1′, 2′, 5, 5′	M	1, 2, 3′, 4′, 5, 5′	3, 4, 1′, 2′, 5, 5′

$\bar{\Sigma}$	1	2	$\bar{\Delta}$	1	2	$\bar{D}$	1	2
Δ, T	1, 2′, 5	1′, 2, 5	Σ	1, 4	2, 3	Z	1, 4	2, 3
Λ	1, 3	2, 3	Δ	1, 2, 5	1′, 2′, 5	T	1, 2, 5	1′, 2′, 5
			Z	1, 3	2, 4			

The (111) face

$\boldsymbol{b}_1 = \frac{2}{3}(2, -1, -1)$, $\boldsymbol{b}_2 = \frac{2}{3}(-1, 2, -1)$

$\bar{\Gamma} = (\gamma, \gamma, \gamma,), \bar{K} = (\gamma + \frac{2}{3}, \gamma - \frac{2}{3}, \gamma), \bar{M} = (\gamma + \frac{1}{3}, \gamma - \frac{2}{3}, \gamma + \frac{1}{3})$

$\bar{T} = (\gamma + \frac{2}{3}\alpha, \gamma - \frac{2}{3}\alpha, \gamma), \bar{T}' = (\gamma + (2 - \alpha)/3, \gamma - \frac{2}{3}, \gamma + \alpha/3)$

$\bar{\Sigma} = (\gamma + \alpha/3, \gamma - \frac{2}{3}\alpha, \gamma + \alpha/3)$

$\bar{\Gamma}_i$ $i = 1, 2, 3$	$\bar{T}$ and $\bar{T}'$	$\bar{\Sigma}$	1	2
Λ_i	Σ, S	Δ, T	1, 2′, 5	2, 1′, 5
		Σ	1, 3	2, 4

$\bar{M}$	1	2
M, X	1, 3, 2′, 4′, 5, 5′	2, 4, 1′, 3′, 5, 5′
Λ (middle)	1, 3	2, 3

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