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Band narrowing and charge transfer in six intermetallic compounds*

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Self-consistent band calculations on six intermetallic compounds of the CsCl structure and on constituent bcc solids with the same lattice spacing show $3d$-band narrowing in the compounds and charge transfer between the compound constituents. The d-band narrowing in the compounds results from a lack of d states on neighboring atoms into which electron tunneling can occur. In the case of compounds with two d-band constituents, we find an additional d-band narrowing due to mutual d-band repulsion. Charge transfers, found by a direct comparison of the charge densities in the compound and in the elemental solid, are always from the element with the higher Fermi energy to the element with the lower Fermi energy.

I. INTRODUCTION

A considerable number of binary intermetallic compounds crystallize in the CsCl structure. The many possible combinations make this group of compounds ideally suited for a systematic study of band structure, density of states, and charge density. In this paper we use self-consistent band calculations to study CuZn, NiZn, AlNi, AlCo, BeCu, and BeCo.

In studying each compound, a series of three independent self-consistent calculations (each involving 20–30 complete iterations) was done. In addition to the calculation of the AB compound, hypothetical bcc AA and BB elemental solid calculations with the same lattice spacing as the compound (the nuclear positions of the CsCl structure constitute a bcc lattice) were executed in order to have a basis for comparison. In this paper we concentrate on $3d$-band narrowing as seen in the density of states and on the charge-density difference for an atom in the compound in the corresponding bcc solid.

The self-consistent calculations, which make use of a fast version[1] of the Korringa, Kohn, and Rostoker[2] (KKR) method, involve two fundamental approximations. First, both the charge density and the effective one-electron potential are spherically averaged inside nonlapping (muffin-tin) spheres and volume averaged in the interstitial region prior to their use in Poisson's and Schrödinger's equations. Second, we use an exchange and correlation treatment identical to Slater and co-workers's[3] $X\alpha$ method except that a single material independent α is used throughout. The specific α used is that which implies the experimental Fermi surface for elemental copper[4] ($\alpha = 0.77$). Theoretically, α is expected to vary smoothly with atomic number.[5] We have used α throughout because the difference between the theoretical and empirical α's for copper is greater than the theoretical variation in α over the entire range of elements studied.

The calculations reported here are an extension of and include our work on β-brass[6] or CuZn. The CuZn results differ from our earlier work only in the value of the muffin-tin radii used. In this work we use equal-volume muffin-tin spheres while unequal-volume spheres were used in our earlier work. The differences in band energies and densities of states are insignificant and CuZn is included here mainly for completeness. Some preliminary charge-transfer results for these compounds have also been reported elsewhere.[7] The present work represents a more detailed study and includes charge transfer as a function of radial position.

The self-consistent band calculations discussed here are appropriate only to the ground state and should not be compared directly with experiment. In order to compare with excited-state properties, a self-energy correction should be applied to all eigenvalues.[8] Our experience with elemental copper and with β-brass indicates that, in order to compare with optical data, the band energies and density of states should be increased by approxi-

TABLE I. Band energies relative to E_f for CuZn (in eV).

Band index	X	Γ	M	R
12	−2.261	>1.195	−1.705	>1.195
11	−3.122	−3.077	−1.705	>1.195
10	−3.548	−3.077	−2.883	−2.864
9	−3.548	−3.077	−3.245	−2.864
8	−4.020	−3.973	−3.245	−4.450
7	−5.253	−3.973	−3.769	−4.450
6	−5.914	−8.423	−4.865	−4.450
5	−8.362	−8.423	−8.213	−8.204
4	−8.562	−8.423	−8.617	−8.204
3	−8.562	−9.008	−8.617	−8.875
2	−8.796	−9.008	−8.835	−8.875
1	−8.855	−9.948	−9.080	−8.875

TABLE II. Band energies relative to E_f for NiZn (in eV).

Band index	X	Γ	M	R
12	−0.139	>3.283	−0.660	>3.283
11	−0.981	−0.935	−1.045	>3.283
10	−1.596	−0.935	−1.045	−0.634
9	−1.596	−0.935	−1.196	−0.634
8	−2.223	−2.204	−1.196	−2.977
7	−4.679	−2.204	−1.981	−2.977
6	−5.095	−7.930	−3.650	−2.977
5	−7.873	−7.930	−7.711	−7.700
4	−8.081	−7.930	−8.140	−7.700
3	−8.081	−8.577	−8.140	−8.420
2	−8.349	−8.577	−8.389	−8.420
1	−8.412	−9.457	−8.624	−8.420

mately (8–10)% when measured relative to the Fermi energy.

II. BAND NARROWING

The band energies (in eV) relative to the respective Fermi energies for the six compounds, at the symmetry points X, Γ, M, and R are summarized in Tables I–VI. CuZn and NiZn each show two sets of d bands while AlNi, AlCo, BeCu, and BeCo each show single set of d bands reflecting the d bands of the constituent atoms. This is most apparent in the density-of-states curves shown in Figs. 1–6. These curves were obtained by a generalization of the method of Gilat and Raubenheimer[9] and are based on calculations done on a uniform k-space mesh of 203 points in the $\frac{1}{48}$th of the Brillouin zone. We show here the density of states for the compound and for the corresponding bcc solids of each d-band constituent. In each case, the zero in energy is the respective muffin-tin zero.

For CuZn and NiZn we see very narrow low-lying Zn d bands in addition to broader d bands near the Fermi energy which are also apparent in AlNi, AlCo, BeCu, and BeCo. In every compound studied we find the same "zone-face" bands reported earlier for the case of CuZn.[6] These bands appear as distinct peaks on each side of the main d-band complexes and are a consequence of band mixing or hybridizing near the Brillouin-zone face defined by symmetry points M, X, and R. These zone-face bands are clearly seen in CuZn and NiZn but the lower component is considerably weakened in the other compounds studied.

As Figs. 1–6 show, each compound studied has d bands which are considerably more narrow than those of the corresponding bcc solid with the same lattice separation. Although a precise measure of bandwidth is arbitrary, we choose to measure our d bands at 20% of peak value. In this manner, we obtain the bandwidths shown in Table VII, where w_E is the d band width in the bcc elemental solid and w_C is the d-band width in the compound. We see that, in every case, the compound has narrower d bands than the elemental solid. If $\overline{w}$ is the average band width, the quantity $(w_E - w_C)/\overline{w}$ can be used as a measure of the band narrowing. Table VII then shows that compounds with two d-band constituents (CuZn and NiZn) show considerably more band narrowing than compounds with

TABLE III. Band energies relative to E_f for AlNi (in eV).

Band index	X	Γ	M	R
9	>2.940	>2.940	+2.381	>2.940
8	>2.940	>2.940	+1.709	+2.137
7	−0.743	>2.940	−1.175	+2.137
6	−1.525	−1.607	−2.111	+2.137
5	−2.267	−1.607	−2.111	−1.146
4	−2.267	−1.607	−2.732	−1.146
3	−2.920	−3.375	−2.732	−4.038
2	−6.577	−3.375	−3.404	−4.038
1	−6.743	−10.880	−5.203	−4.038

TABLE IV. Band energies relative to E_f for AlCo (in eV).

Band index	X	Γ	M	R
9	>3.351	>3.351	+3.314	>3.351
8	>3.351	>3.351	+2.634	+2.518
7	+0.161	>3.351	−0.301	+2.518
6	−0.721	−0.826	−1.449	+2.518
5	−1.641	−0.826	−1.449	−0.264
4	−1.641	−0.826	−2.520	−0.264
3	−2.414	−2.984	−2.520	−3.789
2	−6.374	−2.984	−2.989	−3.789
1	−6.588	−10.751	−5.076	−3.789

TABLE V. Band energies relative to E_f for BeCu (in eV).

Band index	X	Γ	M	R
9	>3.956	>3.956	+3.763	>3.956
8	>3.956	>3.956	+3.101	>3.956
7	−2.033	>3.956	−2.306	>3.956
6	−3.192	−3.245	−2.306	>3.956
5	−3.869	−3.245	−2.858	−2.833
4	−3.869	−3.245	−3.652	−2.833
3	−4.490	−4.754	−3.652	−5.299
2	−5.079	−4.754	−4.472	−5.299
1	−6.792	−10.094	−5.548	−5.299

TABLE VI. Band energies relative to E_f for BeCo (in eV).

Band index	X	Γ	M	R
9	>5.382	>5.382	>5.382	>5.382
8	>5.382	>5.382	>5.382	>5.382
7	+0.471	>4.023	+0.668	>5.382
6	+0.121	+0.027	−0.695	>5.382
5	−1.136	+0.027	−0.695	+0.714
4	−1.136	+0.027	−1.186	+0.714
3	−2.080	−2.580	−1.186	−3.748
2	−4.001	−2.580	−2.133	−3.748
1	−5.680	−9.232	−4.045	−3.748

only one d-band constituent (AlNi, AlCo, BeCu, and BeCo). We also note that the Cu to Zn d-band separation in CuZn is less than the Ni to Zn d-band separation in NiZn and that the band narrowing in the former is somewhat greater than in the latter. This suggests that, for compounds with two d-band constituents, the d-band narrowing increases with decreasing d-band separation.

As a preliminary to the discussion of changes in d-band width due to changes in the atomic environment we recall the origin of the d-band width in the elemental system. The combination of the crystal and centrifugal $[l(l+1)/r^2]$ potentials forms a well-barrier combination which tends to trap and localize the d electrons. The possibility of leaking or tunneling out of the well through the barrier gives the d state a finite width. The depth of the well is proportional to the nuclear charge causing the d-band width to decrease exponentially with atomic number. This decrease can be most clearly seen by comparing the d-band width in Cu and Zn which differs in atomic numbers by only one.

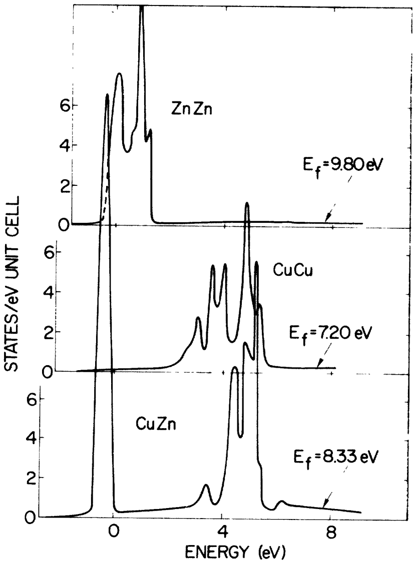

FIG. 1. Density of states for CuZn, CuCu, and ZnZn with a lattice spacing of 5.5819 a.u. E_f is relative to the muffin-tin zero.

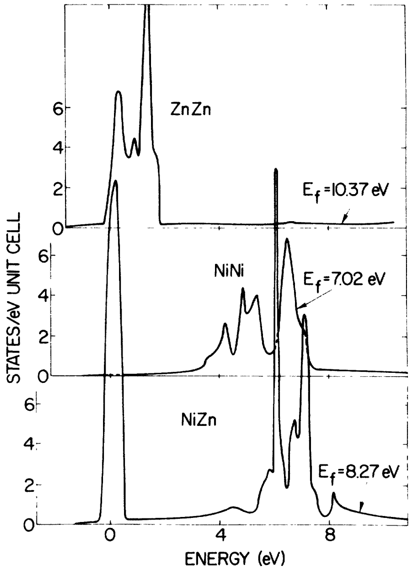

FIG. 2. Density of states for NiZn, NiNi, and ZnZn with a lattice spacing of 5.5703 a.u. E_f is relative to the muffin-tin zero.

Band narrowing in compounds can be explained in terms of the rate at which electrons tunnel through the localizing barrier. The rate at which electrons of a given energy can tunnel from a given site to a nearest neighbor site is proportional to the density of final states at that energy and as-

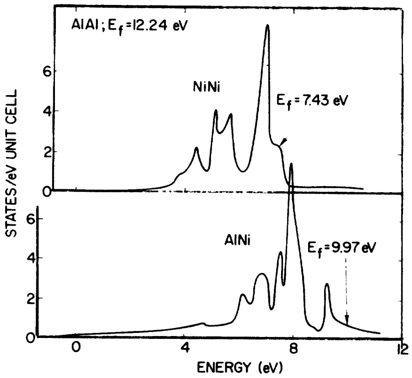

FIG. 3. Density of states for AlNi and NiNi with a lattice spacing of 5.4446 a.u. E_f is relative to the muffin-tin zero.

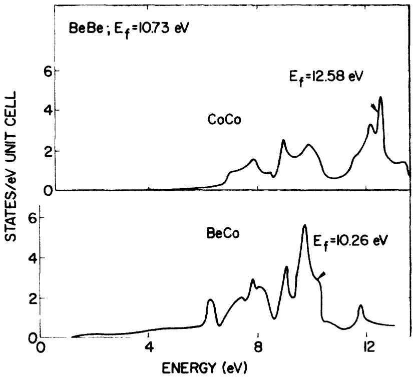

FIG. 4. Density of states for AlCo and CoCo with a lattice spacing of 5.4085 a.u. E_f is relative to the muffin-tin zero.

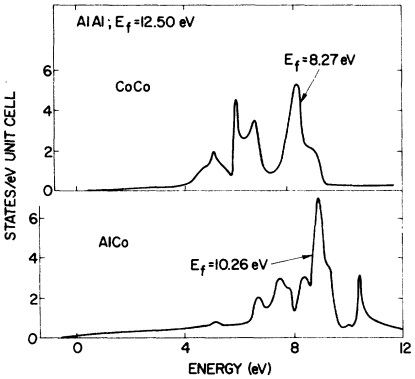

FIG. 6. Density of states for BeCo and CoCo with a lattice spacing of 4.9249 a.u. E_f is relative to the muffin-tin zero.

sociated with the nearest-neighbor site. In the case of the bcc elemental solid, a given atom will have as its nearest neighbor another atom of the same kind. Consequently, there will be a high density of final states for d-electron nearest-neighbor tunneling leading to broad d bands. In the case of the compound, nearest neighbors are replaced by unlike atoms. If there is only one d band, or if two d bands do not overlap, there is a much lower density of final states leading to narrow d bands. Note that the band narrowing described here is not the same as Heine's[10] inverse fifth power band narrowing which is due only to increased atomic separation. (Heine's band narrowing, however, can be seen in our bcc copper results where we find d-band widths of 2.56 eV for $a = 5.5819$ a.u. and 4.22 eV for $a = 5.0987$ a.u. The deviations from a fifth-power rule are due to difficulties in precisely defining band widths.)

The situation for compounds with two d-band constituents is only slightly more complicated. If the energy separation between respective d bands is comparable to the d-band widths themselves, the states will interact. As in any two-state system, the energy levels are repelled by the interaction. Furthermore, the levels in the bands will be spread apart by an amount inversely proportional to their original energy separation. We expect, then, that states which were initially closer together will be spread apart more than those that were initially further apart. That is, the bottom of the higher d band and the top of the lower d band will interact more than the top of the upper band and the bottom of the lower band. The result of this interaction is an additional band narrowing. Thus compounds with two d-band constituents can be expected to have a d-band repulsion narrowing.

This d-band repulsion narrowing is clearly dem-

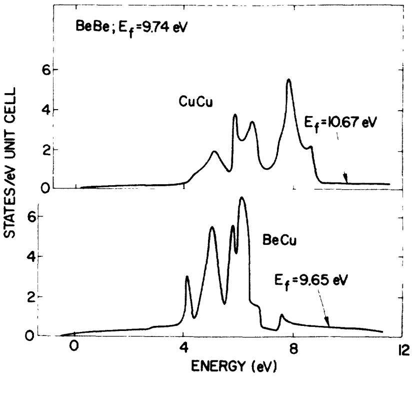

FIG. 5. Density of states for BeCu and CuCu with a lattice spacing of 5.0987 a.u. E_f is relative to the muffin-tin zero.

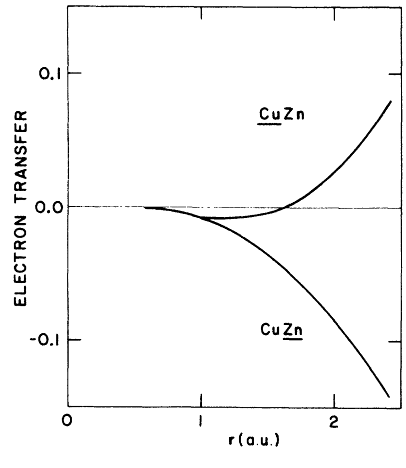

FIG. 7. Charge transfer in CuZn.

TABLE VII. *d*-band narrowing (eV).

Constituent	a (a.u.)	Configuration	w_E	w_C	$(w_E - w_C)/\bar{w}$
Copper	5.5819	CuCu/CuZn	2.56	1.29	0.66
Zinc	5.5819	ZnZn/CuZn	1.63	0.68	0.82
Nickel	5.5703	NiNi/NiZn	3.27	1.82	0.57
Zinc	5.5703	ZnZn/NiZn	1.63	0.75	0.74
Nickel	5.4446	NiNi/AlNi	3.61	2.58	0.33
Cobalt	5.4085	CuCo/AlCo	4.49	2.88	0.44
Copper	5.0987	CuCu/BeCu	4.22	2.58	0.48
Cobalt	4.9249	CoCo/BeCo	6.53	4.26	0.42

onstrated in Figs. 1 and 2 for CuZn and NiZn, while the density-of-final-states effect is in evidence in Figs. 3–6 for AlNi, AlCo, BeCu, and BeCo.

III. CHARGE REDISTRIBUTIONS

The achievement of self-consistency in band calculations permits the unambiguous determination of crystal charge densities subject only to the fundamental approximations (muffin tin and exchange correlation) of the theory. We have computed the charge densities for the six binary compounds listed, as well as for the 12 corresponding bcc elements. We study the difference in charge density between the compound and the bcc elements by forming quantities such as

$$\delta_A(r) \equiv 4\pi r^2[\rho_A^C(r) - \rho_A^E(r)], \qquad (1)$$

where $\rho_A^C(r)$ is the charge density for the A constituent in the compound and $\rho_A^E(r)$ is the charge density for atom A in the elemental solid with the same lattice separation. The results show that, in all cases, the major changes in the charge density occur in the outer regions of the atoms. The differences between the compound and the bcc element arises from a spill over of mobile s and p electrons from one constituent to another.

In Figs. 7–12 we show the integrals of Eq. (1) for the six compounds studied. That is, the curves represent the charge transfer $\Delta(r)$ found by forming

$$\Delta_A(r') \equiv \int_0^{r'} 4\pi r^2[\rho_A^C(r) - \rho_A^E(r)]dr' . \qquad (2)$$

Each figure corresponds to a compound and contains a curve for each constituent, with the labeling such that the constituent being considered appears underscored. Thus we see from Fig. 7,

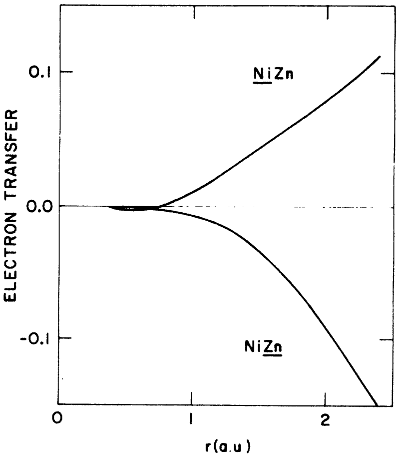

FIG. 8. Charge transfer in NiZn.

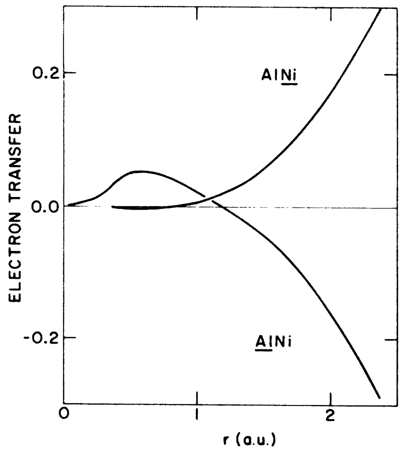

FIG. 9. Charge transfer in AlNi.

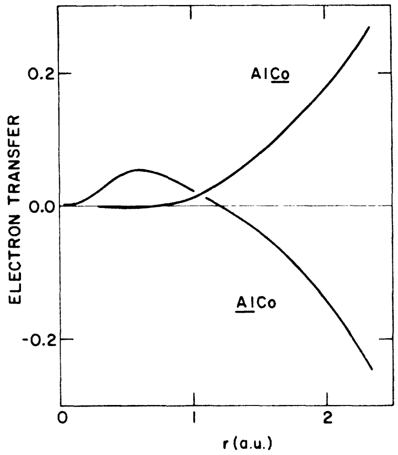

FIG. 10. Charge transfer in AlCo.

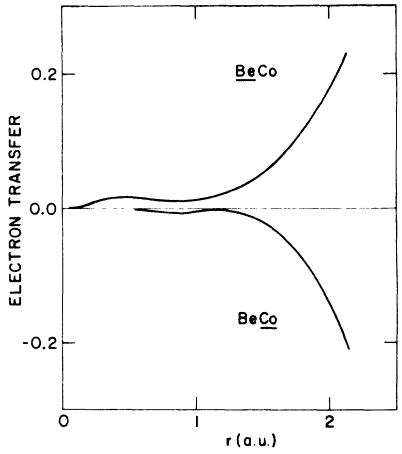

FIG. 12. Charge transfer in BeCo.

for example, that out to 2.4 a.u. (near the muffin-tin radius), copper gains 0.08 electrons and zinc loses 0.14 electrons. The difference (0.06 electrons) is absorbed in the interstitial charge. Note that the difference in interstitial charge (the difference between the interstitial charge for the compound and the sum of the interstitial charges for the two bcc elemental solids) can be either positive or negative.

In every case, the total charge transfer (the charge transfer out to the muffin-tin radius) is from elements on the right-hand side of the Periodic Table to elements on the left-hand side. That is, the charge transfer is Cu ← Zn, Ni ← Zn, Co ← Al, Be ← Cu, and Be ← Co. The charge flow is always from the element with the higher Fermi energy (relative to the muffin-tin zero and not necessarily relative to the bottom of the s band) to the element with the lower Fermi energy. Except for cases involving beryllium, the charge transfer is consistent with Pauling's electronegativity sequence. The contradiction for cases involving beryllium is a consequence of a high effective mass ($m^*/m \approx 1.3$) and correspondingly low Fermi energy for the elemental beryllium calculations.

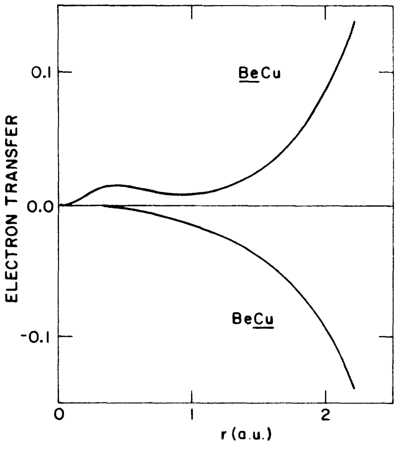

FIG. 11. Charge transfer in BeCu.

The positive core charge transfers for aluminum and beryllium are not considered dependable. They are, to some extent, a consequence of a size effect. Both aluminum and beryllium, which have smaller metallic radii than their companion constituents, are forced, in the bcc calculations, to be larger than they normally would be. Thus, when we form the difference [Eq. (1)], we find an artificial positive core transfer due merely to compression back to a realistic density.

We caution the reader against the use of our calculations to interpret soft x-ray emission data such as that of Wenger, Burri, and Steinemann[11] which includes AlNi and AlCo. There are two important differences between our calculations and the experiments. The calculations discussed here use hypothetical bcc elements as a reference while the reference system for the experiments are the real fcc elements. Moreover, the experiments involve differential measurements which consider only 3d electrons while our calculations give the total charge transfer.

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