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Augmented-Plane-Wave Calculations of the Electronic Structure of Intermetallic Compounds YCu and YZn

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In order to understand the electronic structure of the rare-earth intermetallic compounds RX, where X = Cu, Ag, Au or Zn, Cd and R is a rare-earth element, the energy bands of the isomorphous compounds YCu and YZn have been calculated by the augmented-plane-wave method along different symmetry directions. The calculated Fermi energies for YCu and YZn are +0.42 and +0.47 Ry, respectively. The densities of states $N(E_F)$ at the Fermi level are obtained as 1.9 ± 0.2 and 2.35 ± 0.2 electrons/eV unit cell for YCu and YZn, respectively. This value for YCu is in good agreement with the experimental value of 1.32 electrons/eV unit cell obtained from specific-heat measurements. Also, the calculated change of density of states near the Fermi level is in the same direction as that obtained from specific-heat results on YCu substituted with small quantities of Ni or Zn. The implications of the calculated energy bands are discussed.

I. INTRODUCTION

Considerable experimental work has been done recently on the intermetallic compounds of rare earths with metals of group IB (Cu, Ag, Au) and group IIB (Zn, Cd) having CsCl structure. The principal interest in these studies is to see the effect of the number of conduction electrons on the magnetic ordering. The magnetic properties of these compounds have been studied by Pierre and Pauthenet[1] and by Walline and Wallace[2] for RCu and RAg compounds and by Alfieri *et al.*[3] for RZn and RCd compounds, where R is a rare-earth element. These studies indicate that the ordering changes from antiferromagnetic to ferromagnetic as one goes from compounds of rare earths with monovalent metals (Cu, Ag, Au) to divalent metals (Zn, Cd). However, the analysis of the results in terms of Ruderman-Kittel-Kasuya-Yosida (RKKY) theory[4] requires that the effective parameter K_F be smaller than that deduced from the free-electron model.[5] Neutron-diffraction studies have been made earlier on TbCu, TbAg, TbZn, and ErCu by Cable *et al.*[6] and more recently on HoCu, DyCu, and DyZn by Pierre *et al.*[7] In order to study in detail the change of magnetic ordering, both neutron[8] and magnetic measurements[9] have been made on the solid solutions of rare earths having the general formula $RM_{1x}M_{2(1-x)}$, where M_1 and M_2 represent Cu, Ag, Zn, In, and Ga. Nuclear magnetic resonance of Cu^{63} in RCu compounds have been studied by De Wijn *et al.*[10] and the exchange parameters Js-f have been estimated. These values of Js-f are, in general, larger than those deduced from the magnetic measurements. Mössbauer experiments were done on ErAg by Petrich[11] and on DyCu, DyAg, DyZn, and DyRh by Belakhovsky and Pierre.[12] These studies show that the isomer shift increases on going from DyZn to DyAg and from DyCu to DyRh, indicating that the density of s-like conduction electrons at the Dy nucleus increases in the same order. There is appreciable quadrupole splitting in these cubic systems in the magnetically ordered phase and this arises principally from the $|\frac{15}{2}\rangle$ level of Dy^{3+}, though there is a small decrease from DyCu and DyAg to DyZn, which is presumably due to the change of conduction-electron effect on alloying with monovalent and divalent metals. The electrical resistivity of these compounds has been studied by Chao.[13] The spin-disorder resistivity for RCu and RAg gives an effective mass of the conduction electrons of the order of $3m_e$.[5]

All these studies indicate that the conduction electrons play an important role in the physical properties of these compounds. But a proper interpretation of the effect of conduction electrons on the physical properties of these intermetallic compounds requires a knowledge of the energy bands. Specific-heat measurements have been made at low temperature on the structurally isomorphous but nonmagnetic compounds YCu and YAg[14]; these give values for $N(E_F)$, the density of states at the Fermi level, at least three times greater than the free-electron values. It would therefore be interesting to undertake band calculations in these compounds and interpret the experimental results on the basis of the calculated electronic structure, which is expected to be different from the free-electron model. Here we report the results of such calculations for the β phases of YCu and YZn. Yttrium compounds are expected to have an electronic structure similar to those of the rare-earth compounds; moreover, as Y is nonmagnetic, the magnetic $4f$ electrons do not complicate the problem. We have used the nonrelativistic augmented-plane-wave (APW) method of Slater[15] in the present calculations. The APW method has been used successfully for rare earths by several investigators[16] and also for intermetallic compounds such as β-brass.[17,18] Loucks[19] has calculated the band structure of Y by this method and obtained good agreement with the results obtained by positron-annihilation experiments on this metal. Relativistic effects are important for the rare earths[20] but this effect is expected to be less pronounced for Y than for rare earths and consequently in the present calculations we have followed the nonrelativistic method.

Energy-band calculations in intermetallic compounds have begun only very recently and special attention has been focussed on β-brass[17,18] because experimentally this was well studied by de Haas–van Alphen[20] and optical-reflectance[21] techniques. Both the Korringa-Kohn-Rostoker (KKR)[17] and the APW[18] methods have been used, and the energy bands obtained by the two methods are in fairly good agreement among themselves and also with the available experimental results. No detailed calculations on the intermetallic compounds of rare earths or yttrium have so far been published. So in addition to its experimental relevance, the present investigation on the energy bands of intermetallic compounds of yttrium, and subsequently of rare earths, will be of theoretical interest as well.

II. DETAILS OF CALCULATIONS

Like β-brass both YCu and YZn in their β phases have CsCl structure (see Fig. 1). The two basic shortcomings of the APW method—(i) the neglect of the nonspherical part of the crystal potential and (ii) consideration of the constancy of the crystal potential between the APW spheres—are relatively unimportant for the cubic systems, because, as the symmetry is high, the nonspherical part of the crystal potential is relatively small and so is the volume between the APW spheres, where the approximation of constant potential is used.

The computer programs for these calculations have been derived from the programs of Loucks incorporating two different types of atoms in the unit cell. These programs were written for a IBM 360 computer and can easily be generalized to other cubic structures where the atoms are in positions possessing a real structure factor.

The muffin-tin potential was constructed in the present calculations taking the neutral atomic configurations for the elements, e.g., $4d^1 5s^2$ for Y, $3d^{10} 4s^1$ for Cu, and $3d^{10} 4s^2$ for Zn, as given by Hermann and Skillman.[22] This potential consists of three parts: (i) the Coulomb potential due to the central atom, (ii) the spherically symmetric part of the Coulomb potential due to the neighboring atoms (shells of atoms up to the 14th have been considered), and (iii) the Slater exchange potential given by $V_{ex} = -3\alpha[(3/\pi)\rho(r)]^{1/3}$, where $\alpha = 1$ and $\rho(r)$ is the density of electrons arising from the central atom and the spherically symmetric part of the density due to the neighboring atoms. The radii of the APW spheres were chosen proportional to the metallic radii of the elements. Values of these radii as well as of other crystal parameters used in the calculations are given in Table I. With this choice of the radii of the APW spheres the values of the potentials are nearly the same at the boundaries of the APW spheres. In Fig. 2 we give a plot of the muffin-tin potential as a function of r for YCu. It is seen that the potential becomes nearly constant for r close to R_{APW}, the radius of the APW sphere. The constant potential between the APW spheres was taken as the mean of the two potentials at APW radii. The corresponding potential for YZn is nearly the same with a difference of the order of 3–4% from YCu due principally to the extra $4s$ electron of the Zn atom. The constant potential outside the APW spheres was found to be -1.62 and -1.50 Ry for YCu and YZn, respectively. The origin of the energy scale was adjusted

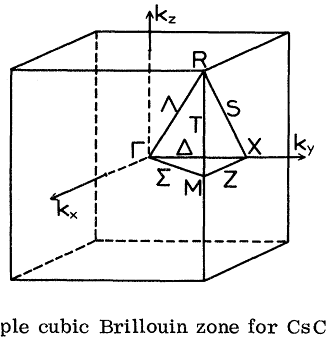

FIG. 1. Simple cubic Brillouin zone for CsCl type of crystal structure and the reduced-symmetry zone.

TABLE I. Values of different parameters involved in the APW calculation for YCu and YZn.

Compound	YCu	YZn
Structure type	CsCl ($B2$)	CsCl ($B2$)
Lattice parameter a	6.557 a.u. (3.470 Å)	6.754 a.u. (3.574 Å)
Yttrium-APW-sphere radius	3.213 a.u.	3.309 a.u.
Copper-(zinc-) APW-sphere radius	2.269 a.u.	2.337 a.u.
Average potential outside spheres	−1.62 Ry	−1.50 Ry

to this value for the subsequent band calculations. The Schrödinger equations corresponding to these muffin-tin potentials were then solved and the logarithmic derivatives of the radial functions were evaluated at R_{APW} for values of l up to 12. The secular determinant was then evaluated taking account of 33 basis functions with the smallest reciprocal-lattice vectors and the energy eigenvalues were obtained for at least 56 nonequivalent wave vectors in the reduced zone, corresponding to 1000 different points in the full Brillouin zone. In general, 10 eigenvalues were determined for each value of the wave vector. Supplementary points were considered along certain symmetry directions to resolve the d-band structure. Except for the d bands which require greater precision, the determinant was calculated in energy steps of 0.005 Ry. The energy bands along some symmetry directions are shown in Figs. 3 and 4 for YCu and YZn, respectively.

For YCu, there is an s-like conduction band at the bottom and then five bands appear in the energy range 0.24–0.32 Ry with widths of the order of 0.08 Ry. Similar to the case of β-brass these can be assigned to the electrons of copper since they have very small bandwidth and are rather sensitive to small variations of the potential inside the copper sphere. Next to the d bands there are bands of somewhat mixed character which should accommodate two more electrons. The widths of these bands are rather large.

For YZn, on the other hand, the d bands are depressed to about −0.22 Ry and their width is of the order of 0.012 Ry. The position of d electrons of Zn is thus similar to that of β-brass. The s-like band is wider than in YCu and spreads 0.02 Ry $[\Gamma_1]$ to 0.36 Ry $[R_{15(25')}]$. The upper bands are not significantly different from those of YCu except that the point R_1 (or $R_{2'}$) is much lower in energy.

On the basis of the eigenvalues found at 56 points in the reduced zone and considering the multiplicity of each of these points we plot the density-of-states histograms for YCu and YZn in Figs. 5 and 6, respectively. For meshes lower than 0.005 Ry the histograms become unstable due to insufficient statistics arising from the limited number of points taken in the Brillouin zone. The density of states for YCu shows a peak around 0.28 Ry with a width of 0.1 Ry which corresponds to ten d electrons of Cu. This lower band also accommodates two s-like electrons, and then a minimum occurs at 0.4 Ry. After this we have bands which are split with a minimum around 0.57 Ry. These bands accommodate the remaining two electrons. The density-of-states curve for YZn is similar to the case of YCu except for the absence of the first peak corresponding to copper d bands since the d electrons of zinc have energies below the conduction bands.

The Fermi energy is then computed by integrating the density of states. The number of occupied states is 7000 and 2500 for YCu and YZn, respectively, since there are 14 and 5 electrons in the conduction bands for the two cases. The computed Fermi energies relative to the bottom of the conduction band (Γ_1 point) are, respectively, +0.42 and +0.47 Ry for YCu and YZn. For YCu, the Fermi energy lies in a region of increasing density of states, whereas in YZn it lies within a region of a broad maximum. We shall discuss the implications of these results in Sec. III.

III. DISCUSSION

We shall first compare the calculated value of $N(E_F)$ in YCu with the value obtained from the specific-heat measurements, namely, 1.32 electrons/eV (all the densities are given for one unit

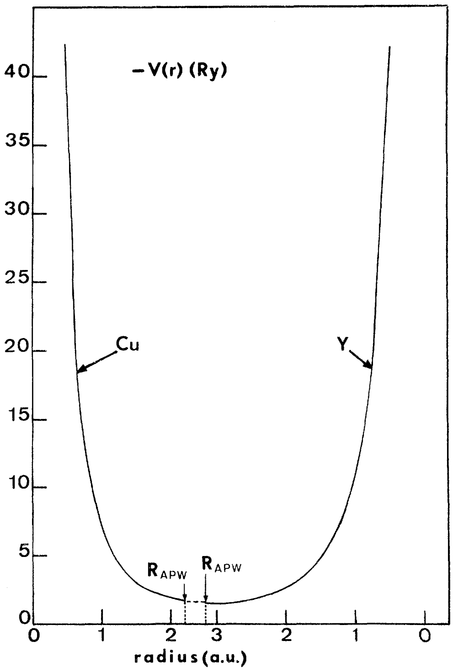

FIG. 2. Muffin-tin potentials in Y and Cu spheres for YCu.

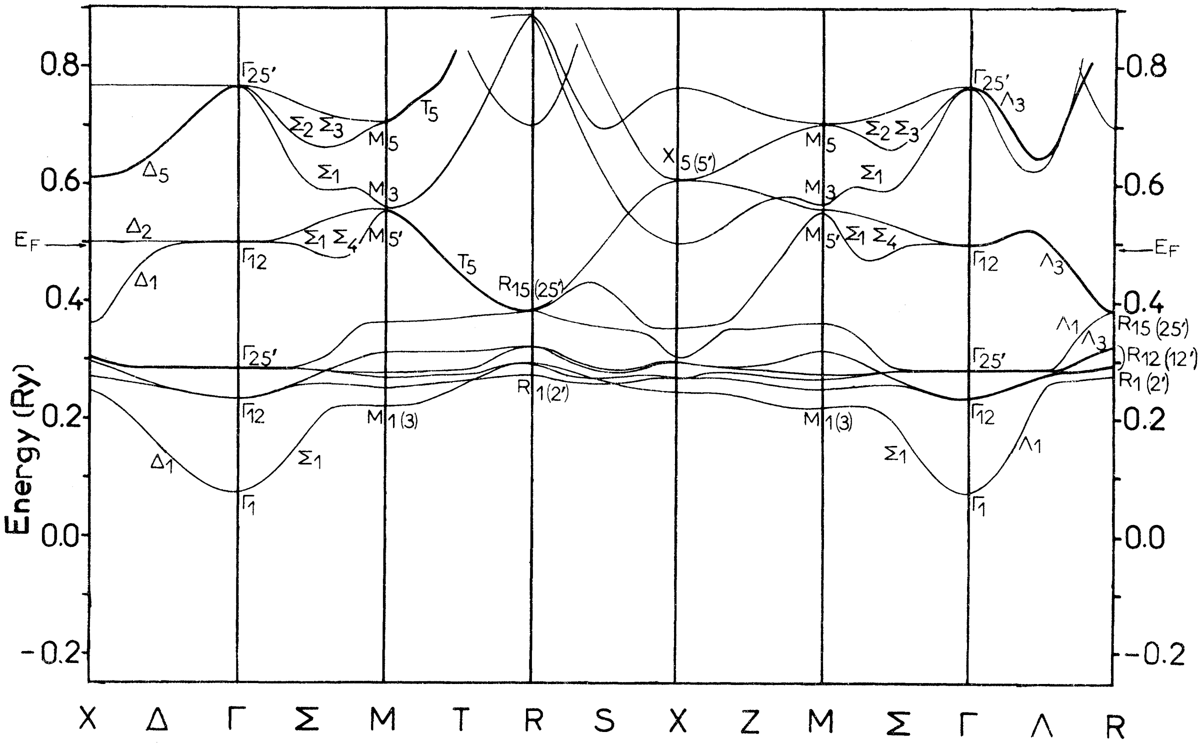

FIG. 3. Energy bands of β-YCu. There are some ambiguities in the labeling of the bands and alternative possibilities are given for a few points.

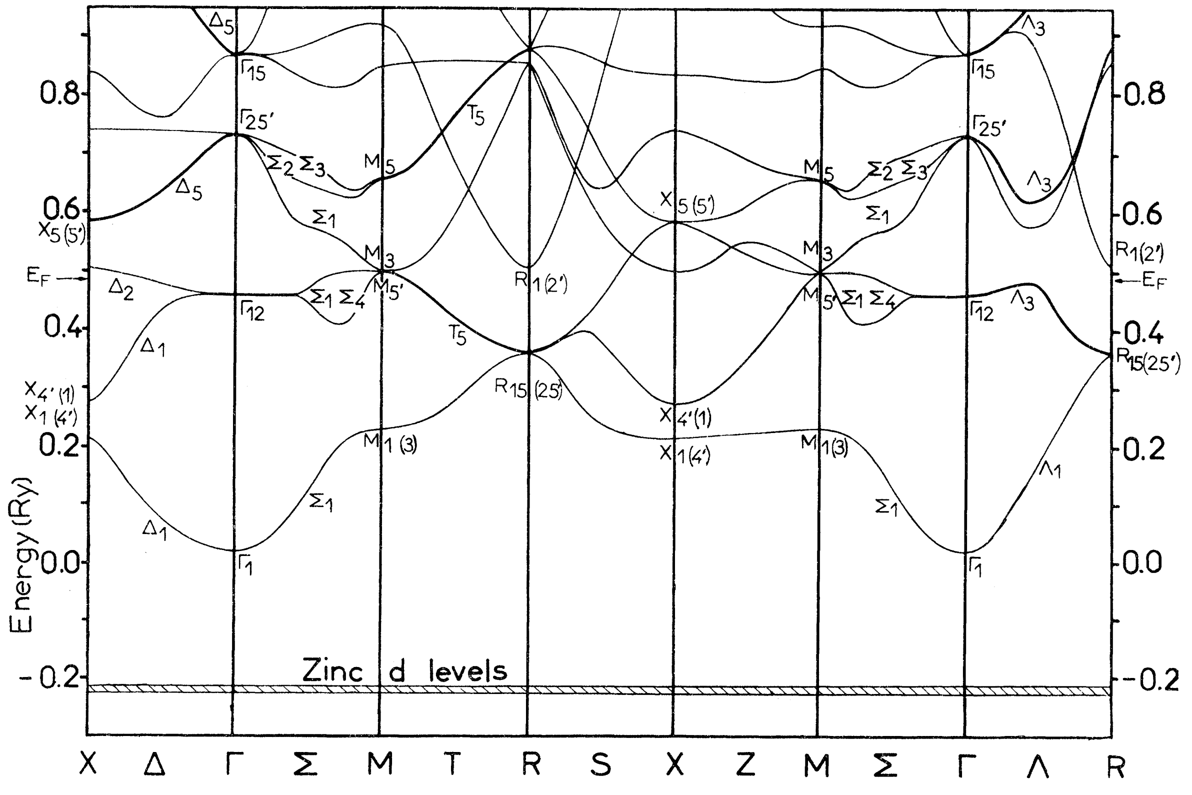

FIG. 4. Energy bands of β-YZn.

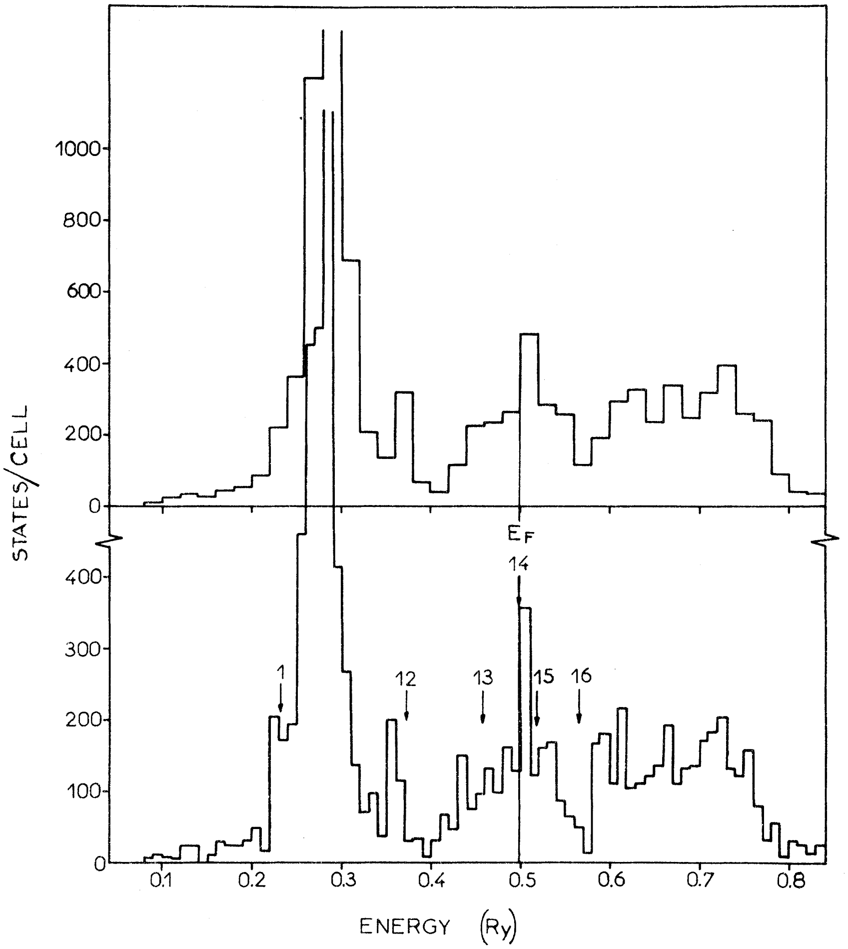

FIG. 5. Density-of-states histogram for YCu. Upper curve: $\Delta E = 0.02$ Ry; lower curve: $\Delta E = 0.01$ Ry. The figures with arrows give the number of electrons in the bands.

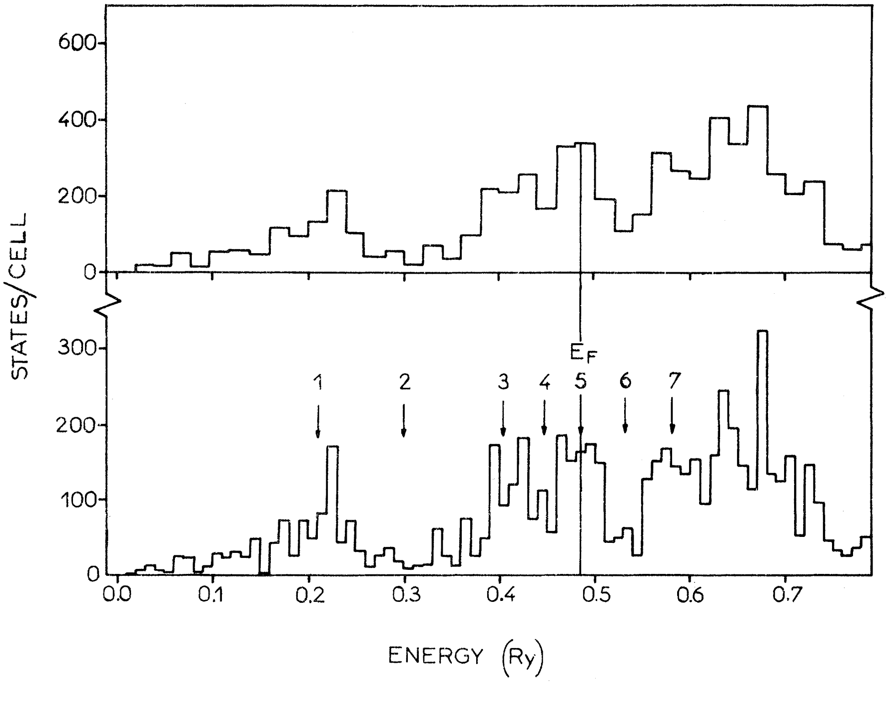

FIG. 6. Density-of-states histogram for YZn. Upper curve: $\Delta E = 0.02$ Ry; lower curve: $\Delta E = 0.01$ Ry.

cell). Using meshes of 0.005 and 0.01 Ry we find for $N(E_F)$ 1.9 ± 0.2 electrons/eV. From the free-electron model, taking into account four valence electrons for YCu, we find the density of states at the Fermi surface to be 0.39 electrons/eV, i.e., nearly three times smaller than the experimental value. The agreement between our calculated value and the experimental value is fairly good in view of the approximation involved in the band calculation. It may be remembered in this connection that for the case of La metal the experimental value of $N(E_F)$ is 4 electrons/atom eV.[23] The theoretically calculated value was 1.4 electrons/atom eV.[24] No experimental result for $N(E_F)$ in YZn is available but specific-heat experiments have been performed with substitution of other metals in place of copper in order to see the effect of the number of conduction electrons on $N(E_F)$. From the results of $N(E_F)$ for $YCu_{0.9}Ni_{0.1}$, $YCu_{0.9}Zn_{0.1}$, and $YCu_{0.8}Zn_{0.2}$, the density increases at the rate of 0.8 (electrons/eV) per number of added electrons. The theoretical value of $N(E_F)$ for YZn is about 2.35 ± 0.2 electrons/eV. This value is not much different from what one expects from the above increase of the density.

If we try to increase the number of electrons in the lattice by alloying with a trivalent metal such as Al, Ga, or In, we see that the Fermi level will fall in a region where the density of states is small and so the total energy of the electronic system will increase. Consequently, the CsCl structure is not likely to be retained. In fact, this happens to be true. For instance, in RAl[25] compounds, the structure is built from half-cells of CsCl structure but arranged in a different manner.

We shall now discuss the different approximations involved in the APW method as employed here. First, the average potential between the APW spheres was taken to be the mean of two slightly different values at the APW radii of yttrium and copper or zinc. Since the number of grid points between the radii of the APW and Wigner-Seitz spheres is not large in our calculation, the procedure suggested by Loucks[19] to calculate the average potential was not found to be suitable. In order to see how much effect a slightly modified value of V_{av} has on the energy bands, we calculated the bands along ΓX direction taking for YCu $V_{av} = -1.4$ Ry instead of -1.62 Ry, and the corresponding results are shown in Fig. 7. The most important change is the location of the d bands of copper, which were lowered by 0.03 Ry with respect both to the Fermi level and to the lowest band Δ_1. But there is no significant over-all change. Second, we have used the neutral configuration for the atoms. It would be necessary to test the validity of this approximation by calculating the charge inside the APW spheres. But it should be mentioned here that the neutral configuration has proved to be a good approximation for β-brass where the net transfer of electronic charge from Cu to Zn is of the order of 0.07 electron. Nevertheless, we have calculated the muffin-tin potential for both Y^+Cu^- and Y^-Cu^+ configurations, taking into account the Ewald potential. Large discontinuities in the potential were introduced for these configurations indicating that the ionicity cannot be so high. An estimation of the ionicity on the basis of the energy bands we have calculated, and then the reconstruction of the muffin-tin potential will be undertaken in future.

Third, we have considered the exchange potential to be of Slater type with $\alpha = 1$. From an analysis of the effect of different expressions for the exchange potential on the energy levels of Cu^+ ion Slater *et al.*[26] have suggested that in band calculations of solids one might have to take α slightly smaller than 1. Recently Shurtleff and Kleinman[27] have considered the effect of exchange potential with $\alpha = \frac{7}{9}$ and $\frac{2}{3}$ on the energy bands of γ-Fe and have come to the conclusion that $\alpha = 1$ gives the best description of the energy bands but $\alpha = \frac{2}{3}$, which was first suggested by Kohn and Sham,[28] gives a better cohesive energy of the crystal. In order to see how far the energy bands in YCu and YZn are sensitive to the choice of the exchange potential we calculated the energy bands of YCu and YZn along ΓX direction for $\alpha = \frac{7}{9}$ and $\frac{2}{3}$ in addition to $\alpha = 1$ which we have discussed earlier. The results indicate that though the nature of the bands other than the d bands of copper or zinc are not altered drastically, the latter bands are pushed

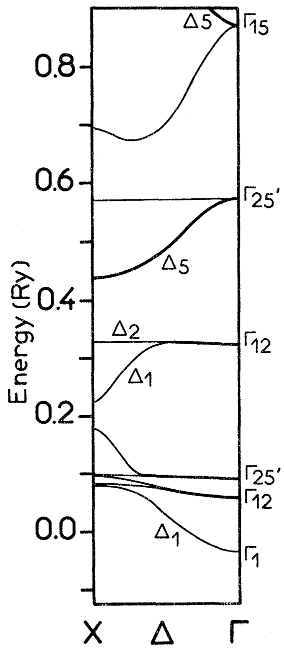

FIG. 7. Energy bands of β-YCu along ΓX direction for a constant potential $V_{av} = -1.4$ Ry.

up enormously. Even for $\alpha = \frac{7}{9}$, the d bands lie near the Fermi level and are partly unfilled, and consequently these compounds would be magnetic, which is contradicted by the nonmagnetic character of these compounds. So α for both YCu and YZn should be close to unity. Optical-reflectance or photoemission experiments would be able to give the position of the d bands with respect to the Fermi level and correspondingly fix the exact value of α.

We therefore conclude that the present calculations give a good description of the energy bands of YCu and YZn. Further calculations on the basis of a self-consistent muffin-tin potential are being carried out for these compounds and on the basis of these results APW calculations of energy bands and electronic functions for RCu and RZn will be undertaken in the future.

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