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Electrons in partially ordered alloys— $\text{Ag}_{0.5}\text{Zn}_{0.5}$

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Abstract. We have calculated the electronic structure of $\text{Ag}_{0.5}\text{Zn}_{0.5}$ in both its ordered (CsCl) phase and substitutionally disordered (BCC) phase. We present the densities of states, k -resolved spectral densities and Fermi surfaces of both phases, and discuss the combined effects of disorder and changing symmetry. We comment on how electronic experiments can monitor changes in the spectral density through the order–disorder transition.

1. Introduction

Great progress in understanding the electronic properties of substitutionally disordered alloys has been made in the last decade, largely as a result of the development of realistic first principles descriptions of the perfectly random model (Faulkner and Stocks 1980, Stocks and Winter 1984). But real alloys, like other types of disordered system, are never completely random. Even in homogeneous solid solutions intersite concentration correlations are generally present and can often be seen as diffuse scattering in diffraction data. In some cases this short-range order becomes stronger as the temperature is lowered and a phase transition to an ordered compound occurs. In such cases the long-range-order (LRO) parameter, S , is related to the concentration of the low-temperature phase on each of the sublattices. In perhaps the simplest of such cases, the A2(BCC) to B2(CsCl) ordering transition occurring in, for example, β -brass (CuZn), S is given by

$$S = C_A^1 - C_B^1 = C_B^2 - C_A^2$$

where C_α^i is the concentration of α -type atom ($\alpha = \text{A}$ or B) on the i th simple cubic sublattice ($i = 1$ or 2) of the B2 structure. Well above the transition temperature $S = 0$, ($C_A^i = C_B^i$), and the two sublattices are equivalent giving A2 symmetry on average. At $T = 0$, $S = 1$ and the system is perfectly ordered in the B2 structure. This particular transition is of second order (this is not always the case; for example, the Cu_3Au ordering transition is of first order). Therefore, just below the ordering temperature S is small but finite and one can picture the system as two interpenetrating substitutionally disordered simple cubic lattices with slightly different compositions. In this sense an ordering alloy at a finite temperature below its phase transition is partially ordered.

From the theoretical point of view it is interesting to study the evolution of the electron states as a function of S , from the homogeneously disordered phase to the

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perfectly ordered one, at a constant overall concentration. This is complementary to the more common procedure of studying the electronic structure of the homogeneous random model as a function of concentration between the limiting ordered cases of pure A and pure B. This corresponds to exploring the phase diagram by varying the composition at a constant (high) temperature, while the former procedure mimics varying T at a constant composition.

The phase diagrams of alloys such as CuZn are usually explained by means of a model configurational Hamiltonian containing pair-wise (and possibly multi-site) interaction parameters. The mean field theory for this model usually gives a reasonable account of the phenomenology of ordering, but more sophisticated statistical treatments are frequently used (eg. De Fontaine 1979). The origin of the interatomic interactions is, however, undoubtedly electronic, and it is the electronic states that determine their strength and range. This implies that the electronic spectral density must be sensitive to the structure in general and to the state of order in particular. First principles electronic theories of phase stability in alloys must be able to describe this structure sensitivity in quantitative detail. In partially ordered alloys this means that one must be able to perform reliable calculations of the dependence of the average spectral density on the LRO parameter S . This is the aim of the present work.

In this paper we describe some calculations on $\text{Ag}_{0.5}\text{Zn}_{0.5}$ alloy which undergoes a second-order A2–B2 ordering transition of the β -brass kind at $T = 600$ K. (We were motivated to study AgZn rather than CuZn because the lower transition temperature makes spectroscopic experiments for varying S somewhat easier to perform; (see Jordan *et al* 1989)). The electronic structure of the A2 disordered system was calculated by the KKR CPA method (Stocks and Winter 1984, Temmerman and Szotek 1987) while the band structure of the ordered compound was determined by the SCF LMTO technique (Skriver 1984); details are given in § 2. These cases correspond to the limits $S = 0$ and $S = 1$ respectively. In § 3 we describe the results for the density of states, the k -resolved spectral density and the Fermi surfaces. The rather striking differences between the two phases are discussed particularly in terms of random hybridisation and the strong s-wave scattering on the Zn sites. In a future paper we will explore the evolution of the electron states of the disordered phase ($S = 0$) into those of the ordered compound ($S = 1$) by performing two-sublattice KKR CPA calculations (Pindor *et al* 1983) for the partially ordered ($0 < S < 1$) alloys.

2. Computational details

The ordered phase was examined using a self-consistent field LMTO ASA calculation. The initial charge density was formed as a superposition of atomic charge densities, which were calculated within the local density approximation using the von Barth and Hedin expression for the exchange and correlation potential (von Barth and Hedin 1972). With frozen core charge densities, self consistency was achieved in 15 iterations and the charge transfer was very small (0.08 electrons), in agreement with the lack of core-level shifts found by Jordan *et al* (1989). Minimising the total energy with respect to the Wigner–Seitz radius of the atomic spheres (figure 1) reproduced the experimental lattice parameter to within about one per cent. We therefore believe that the self-consistent potentials provide an accurate description of the bonding in the ordered alloy.

The disordered phase was examined using the coherent potential approximation (CPA) within the framework of the KKR band theory (that is the KKR CPA). The KKR CPA

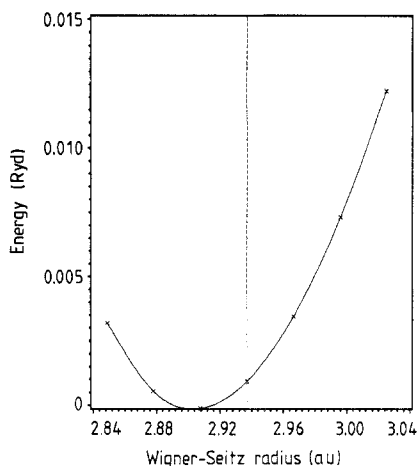


Figure 1. The total energy versus the Wigner-Seitz radius for ordered $\text{Ag}_{0.5}\text{Zn}_{0.5}$. The broken line shows the Wigner-Seitz radius corresponding to the experimental lattice parameter.

is a reliable *ab initio* method for calculating the electronic structure of disordered alloys; it accurately describes both the energetic and the spectroscopic properties of alloys (Stocks and Winter 1984, Györfy 1987, Jordan and Durham 1987). The CPA is a mean-field approximation to the configurationally averaged single-particle Green function of the disordered medium. The occupation of each unit cell in the alloy is assumed to be a random variable (that is, there are no short-range correlations between atoms) and the disorder is treated in a self-consistent manner typical of a mean-field approximation. In the $S = 1$ limit the KKR CPA reduces to the KKR method for ordered compounds, and is in this sense on the same footing as KKR band theory. The KKR CPA also takes into account the site-diagonal, off-diagonal, and random hybridisation effects of the disorder at the same level of approximation, in contrast to the tight-binding implementation of the CPA. Many of the results we present in this paper are predictions of the electronic structure and related properties of $\text{Ag}_{0.5}\text{Zn}_{0.5}$ in its ordered and disordered phases. The gross features of the densities of states, however, have been checked against x-ray photoemission experiments (Jordan *et al* 1989).

The self-consistent potentials generated for the ordered phase were also used in the disordered-phase calculation. In view of the negligible charge transfer in the ordered phase it was not considered necessary to take the disordered calculation to self-consistency within respect to the potential. Note that in a calculation of the total energy of the alloy self consistency would be of greater importance.

3. Results and discussion

In figure 2 we show the scattering phase shifts of the self-consistent potentials. The d resonances are the dominating feature for both silver and zinc, and the energy gap of 0.24 Ryd between the resonances (compared to 0.44 Ryd in CuZn) leads us to expect a split-band alloy somewhat like CuZn (Temmerman *et al* 1988). The zinc d resonance is very sharp compared to the silver d resonance (indeed it is nearly a bound state) and one expects the alloy to have narrow zinc d bands just above the muffin-tin zero, and separate,

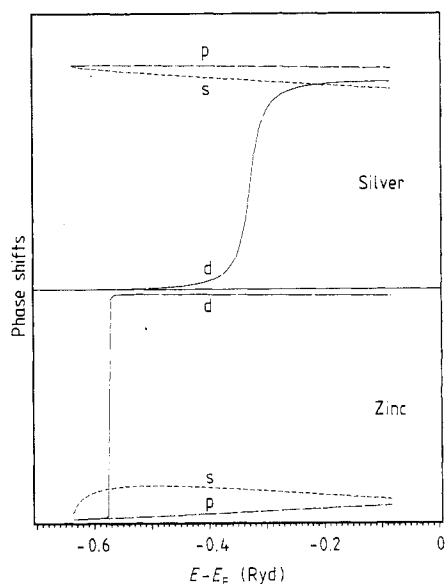


Figure 2. The scattering phase shifts of the potentials at the silver and zinc sites.

broader, silver d bands at higher energy. An interesting feature in figure 2 is the s-phase shift on the zinc site, which is much larger than those usually found in transition metals, and actually much larger than that on the silver site. As we shall see, this s-wave scattering has an important role to play in the electronic structure of the alloy.

3.1. The density of states

Figure 3 shows the densities of states for ordered AgZn, pure Ag and pure Zn. The split-band nature of the alloy is evident, with 0.2 Ryd separation between the d bands. Also the alloy d bands show very little shift in energy relative to the pure components, reflecting the very small charge transfer between alloy sites. The d band widths are smaller in the alloy than in the pure components. This is simply because the width of each sub-band is dominated by overlaps between d orbitals of the same species (due to the large energy splitting between the d bands) and in the B2 structure all nearest neighbours are of unlike species.

Figure 4(a) shows a symmetry decomposition (s, p, d) of the density of states for the disordered alloy. Here in the BCC structure there is 50% likelihood of finding a neighbour of a like species (off-diagonal disorder). Therefore the average overlaps are larger and the d bands are broader than in the ordered case. All of these features have been confirmed in recent XPS measurements.

A symmetry decomposition of the density of states of the ordered alloy is shown in figure 4(b). The sharp feature at -0.43 Ryd has no corresponding feature in either the pure components or the disordered alloy; it lies between the split d bands and has mixed d and s character. We believe that this feature arises from hybridisation between the d states on the silver site and the s states on the zinc site. In order to confirm this we performed a calculation in which the density of states was regenerated, with the LMTO structure-constant matrix altered to prevent the silver-site d symmetry component from

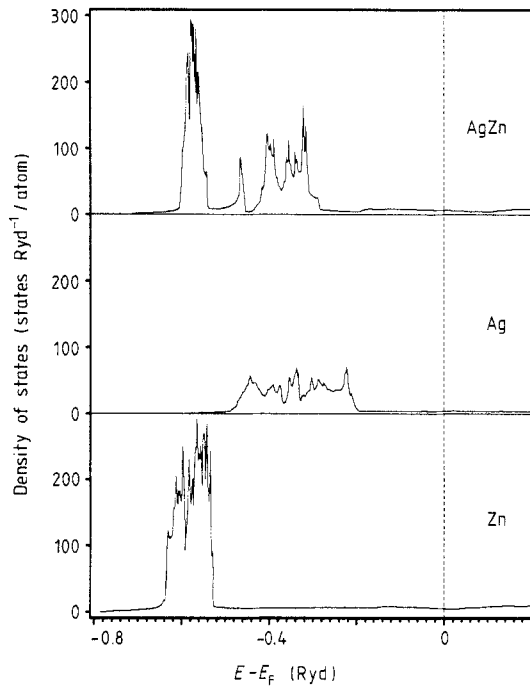


Figure 3. The density of eigenstates in $\text{Ag}_{0.5}\text{Zn}_{0.5}$, Ag (FCC) and Zn (HCP).

interacting with the zinc-site s symmetry component. The resulting density of states is shown in figure 4(c). The feature is no longer present but otherwise the density of states is very similar to that in figure 4(b). The hybridisation is a direct consequence of the strong s scattering on the Zn sites and d scattering on the Ag sites. This is present in the disordered alloy too, of course, but produces no strong feature in the average density of states—random hybridisation is insufficient to split bands in this system.

3.2. The band structure and Bloch spectral functions

In this section we present the ordered band structure, and the Bloch spectral functions, $A_{\mathbf{B}}(\mathbf{k}, \varepsilon)$. The Bloch spectral density is the probability of finding an electron with Bloch momentum and energy in the range; $\mathbf{k} \rightarrow \mathbf{k} + d\mathbf{k}$, $\varepsilon \rightarrow \varepsilon + d\varepsilon$ in the disordered solid (Faulkner and Stocks 1980). In the ordered limit ($S = 1$) it reduces to the energy bands, $A_{\mathbf{B}}(\mathbf{k}, \varepsilon) = \sum_{\nu} \delta(\varepsilon - \varepsilon_{\nu}(\mathbf{k}))$ and is thus the analogue of the band structure in the disordered system.

The band structure of ordered AgZn for the symmetry directions Δ , Σ , and Λ is shown in figure 5. We note that the individual Ag and Zn d -band complexes are well separated in energy, and in fact look almost identical to those of simple cubic Ag and Zn.

In figure 6 we show the spectral function at the Γ point in the disordered phase. Note the ordering of the e_g and t_{2g} states in the two phases. The disordered system has the e_g states higher in energy, a characteristic of the BCC (and FCC) structures related to the fact that the e_g orbitals point towards next-nearest-neighbour atoms. In the ordered system the e_g states are the lower in energy, because in the B2 structure the e_g orbitals on Ag

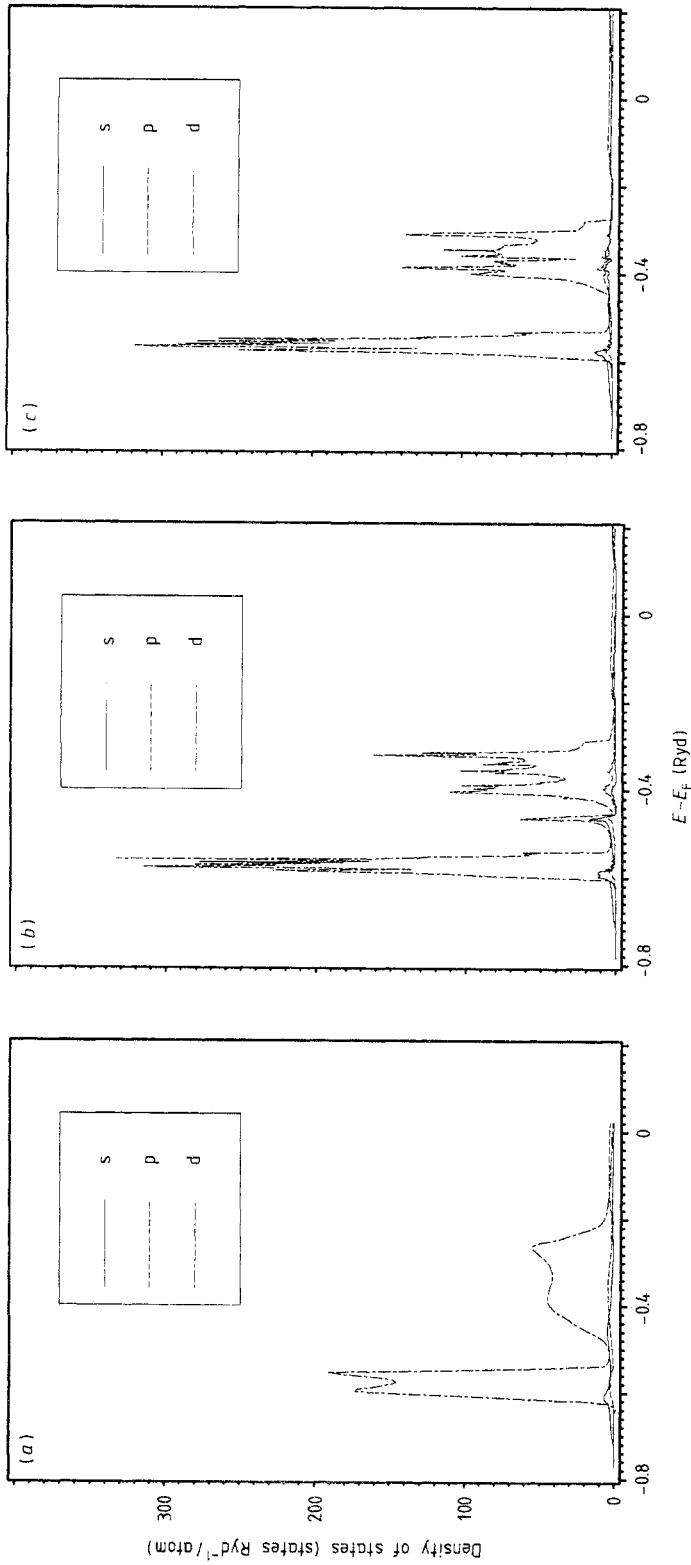


Figure 4. The symmetry-decomposed density of eigenstates in (a) disordered ($S = 0$) $\text{Ag}_{0.5}\text{Zn}_{0.5}$ (b) ordered ($S = 1$) $\text{Ag}_{0.5}\text{Zn}_{0.5}$ (c) ordered ($S = 1$) $\text{Ag}_{0.5}\text{Zn}_{0.5}$ with $\text{Zn}(s)\text{-Ag}(d)$ hybridisation suppressed.

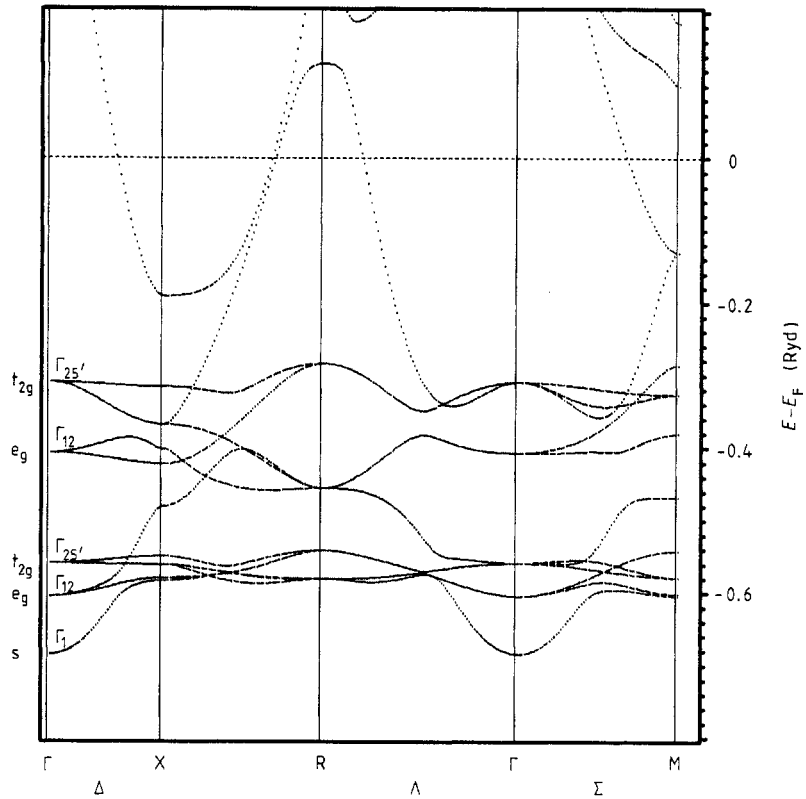


Figure 5. The band structure of ordered $\text{Ag}_{0.5}\text{Zn}_{0.5}$.

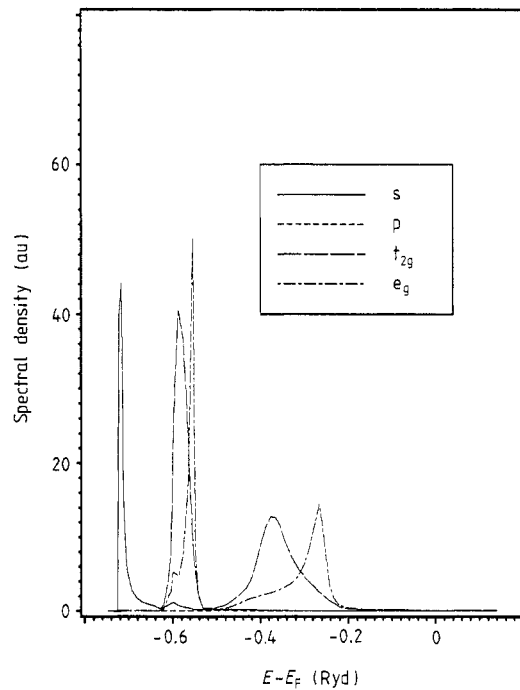


Figure 6. The symmetry-decomposed spectral density, $A_B(k, \epsilon)$, at $k = (0, 0, 0)$ in disordered (bcc) $\text{Ag}_{0.5}\text{Zn}_{0.5}$. Note the energy ordering of the t_{2g} and e_g peaks.

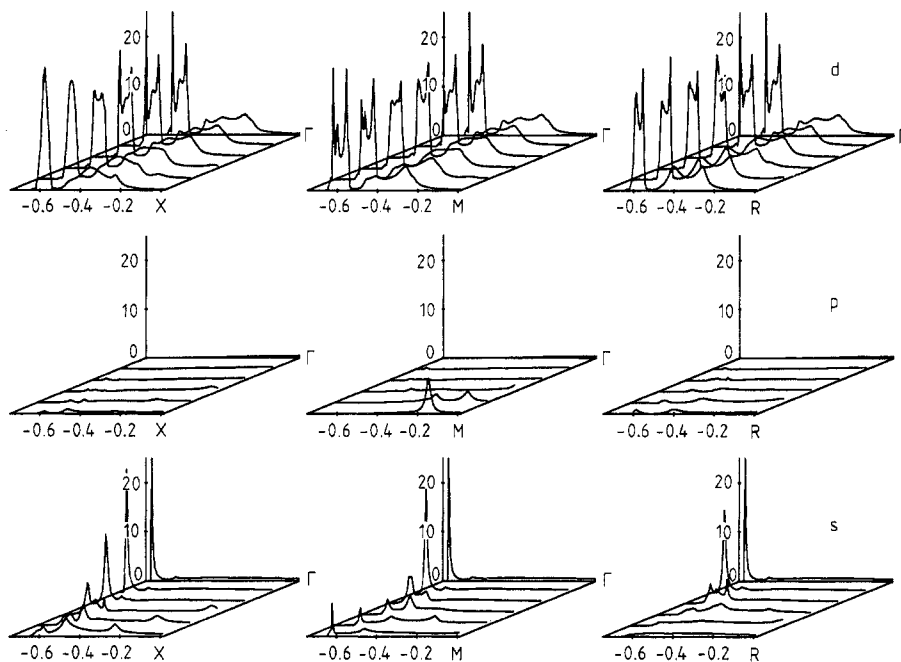


Figure 7. The symmetry-decomposed spectral density, $A_B(k, \epsilon)$, plotted against energy (in Rydbergs), for the Δ , Σ and Λ directions in disordered $\text{Ag}_{0.5}\text{Zn}_{0.5}$, projected into the simple cubic Brillouin zone.

(say) point towards nearest-neighbour Ag atoms, just as they would in simple cubic Ag. It is interesting to speculate how this topological difference in the eigenvalue spectrum develops continuously as a function of S ; we shall look at this in a future publication.

The symmetry-decomposed (s, p and d) spectral functions for the disordered phase ($S = 0$) along the Δ , Σ and Λ directions are shown in figure 7. The spectral functions were calculated for the BCC space group and projected back into the SC Brillouin zone to facilitate comparison with the ordered bands in figure 5. This representation corresponds physically to an infinitesimal value of S . Examining these figures we see that the disorder has not changed the gross features of the electronic structure. There are still two distinct sets of d bands associated with the Ag and Zn sites, and the dispersion of the corresponding peaks is typical of a BCC transition metal. The disorder broadening varies between states of different character. As the phase shifts in figure 2 show, d electrons see a highly disordered array of scatterers, while s and p electrons are scattered more similarly by the two potentials. This leads to the stronger broadening of d bands relative to sp bands, which is a common feature of transition metal alloys. Although the difference between the s-wave phase shifts is uncommonly large in AgZn, it is insufficient to split the wide sp bands.

We turn now to the question of random s–d hybridisation. In an ordered system s–d mixing gives rise to non-crossing rules which tend to expel spectral density of s character from the energy range occupied by the d bands. In a disordered system this effect is modified in such a way that the average spectral density splits into two components, one of which is pushed out of the d-band range (as in an ordered system), while the other actually disperses through the d states, becoming strongly broadened as it does so. This

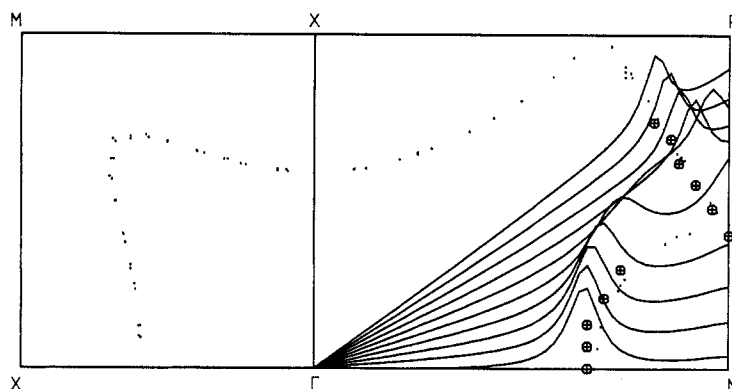


Figure 8. The Fermi surface of $\text{Ag}_{0.5}\text{Zn}_{0.5}$ in both the ordered and disordered phase. The small dots are a projection of the ordered Fermi surface onto the ΓMX , ΓXR and ΓRM planes. The full curves are the Fermi energy spectral function, $A_{\text{B}}(\mathbf{k}, \epsilon_{\text{F}})$, evaluated along rays from the Γ point to the Brillouin zone boundary and the crosses show the positions of the peaks along these rays.

behaviour has been observed in angle-resolved photoemission experiments (Allen *et al* 1983), and can be seen in the spectral functions in figure 7. In most transition metal alloys, because of the general weakness of s-wave scattering, it has not been necessary to distinguish site-diagonal and off-diagonal randomness in the s–d hybridisation. In AgZn , however, we have seen that the $\text{Zn}(s)\text{--Ag}(d)$ mixing is particularly strong, and induces a clear band splitting in the ordered state. In figure 5, the corresponding energy bands occur at about -0.43 Ryd, and can clearly be identified in the Σ direction. These bands disappear when the $\text{Zn}(s)\text{--Ag}(d)$ Hamiltonian matrix element is turned off, as in figure 4(c). This enforced suppression of hybridisation appears to mimic the random hybridisation that comes about when the system disorders; no strong split-off features are visible in the spectral functions (figure 7) at the expected energies. Thus, in the fully random state the effects of even strong off-diagonal hybridisation are highly smeared out, but must gather strength as the long-range order increases.

Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) provides a detailed probe of the spectral densities described above (Jordan and Durham 1987) and we would expect all of the features described above to have consequences for the photocurrents. Temmerman *et al* (1988) showed that for the similar CuZn system the strong effects of ordering on the d bands are clearly visible in theoretical ARUPS spectra. They also showed that positron annihilation measurements will be less sensitive to ordering in CuZn because the positron annihilates mainly with the s electrons. In AgZn the strong changes associated with $\text{Zn}(s)\text{--Ag}(d)$ hybridisation may show up more clearly in positron annihilation data.

3.3. The Fermi surface

The Fermi surface of the ordered phase for the planes ΓMR , ΓXR and ΓXM is shown in figure 8. At the Fermi energy the bands have predominantly sp symmetry and a nearly quadratic dispersion relation (see figures 5 and 7). The Fermi energy spectral function $A_{\text{B}}(\mathbf{B}, \epsilon_{\text{F}})$ of the disordered phase is also shown for the ΓMR plane. The complex shape

of the surface in figure 8 is caused by the folding of the almost spherical surface of the BCC space group back into the first Brillouin zone of the SC space group.

It is immediately apparent that the Fermi surface is still fairly well defined in the disordered phase. However, in view of their essentially free-electron character, the fermi energy states suffer a surprising degree of broadening, certainly more than that found on the s-p sheets of the Fermi surface in Cu-Ni or Ag-Pd alloys (Gordon *et al* 1981). The s and p phase shifts on each site are actually somewhat different near ϵ_F , and while disorder scattering cannot split the s-p band it does produce sizeable broadening. The associated finite mean free path will be apparent in measurements of the residual resistivity and low-temperature specific heat capacity of the alloy, and we shall show in a future paper how these quantities behave for immediate values of S . The loci of the peaks of the disordered Fermi surface are also shown in figure 8, demonstrating that the ordering process does not significantly alter the shape of the Fermi surface. No obvious nesting features are found in the disordered phase.

4. Conclusion

We have investigated the electronic structure of $\text{Ag}_{0.5}\text{Zn}_{0.5}$ in both its ordered and disordered phases using the LMTO and two-sublattice KKR CPA techniques. The density of eigenstates, Fermi surface and Bloch spectral density (in particular its topology), depend on the state of order to varying degrees, with implications for the spectroscopic (ARUPS, positron annihilation, AES, . . .), transport (thermal conductivity, electrical resistivity, . . .) and bonding properties of the alloy. In particular it is tempting to speculate on the role of the Zn(s)-Ag(d) hybridisation feature in the bonding of the alloy, especially in the absence of any obvious ordering features at the Fermi surface. The evolution of the electronic structure as a function of the long-range-order parameter will be examined in a further publication.

References

- Allen N K, Durham P J, Györfy B L and Jordan R G 1983 *J. Phys. F: Met. Phys.* **13** 223
Faulkner J S and Stocks G M 1980 *Phys. Rev. B* **21** 3222
De Fontaine D 1979 *Solid State Phys.* **34** 73-274 (New York: Academic)
Gordon B E A, Temmerman W M and Györfy B L 1981 *J. Phys. F: Met. Phys.* **11** 821
Györfy B L 1989 *Alloy Phase Stability* (Nato ASI Series E, vol 163) (Dordrecht: Kluwer Academic)
Jordan R G and Durham P J 1989 *Alloy Phase Stability* (Nato ASI Series E, vol 163) (Dordrecht: Kluwer Academic)
Jordan R G, Zehner D M, Harrison N M and Durham P J 1989 *Z. Phys.* at press
Pindor A J, Temmerman W M and Györfy B L 1983 *J. Phys. F: Met. Phys.* **13** 1627
Skriver H L 1984 *The LMTO Method* (New York: Springer)
Stocks G M and Winter H 1984 *The Electronic Structure of Complex Systems* (Nato ASI Series B, vol 113) (London: Plenum)
Temmerman W M and Szotek Z 1987 *Comput. Phys. Rep.* **5** 173
Temmerman W M, Durham P J, Szotek Z, Šob M and Larsson C G 1988 *J. Phys. F: Met. Phys.* **18** 2387