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The long-period superlattice in CuAu II

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Abstract. We report the results of a series of calculations of the electronic structure of ordered, equi-atomic CuAu. We have investigated the effects of the creation of superzone boundaries on the Fermi surface of CuAu I when the long-period superlattice, the CuAu II phase, is formed. The new boundaries destroy appreciable regions of Fermi surface, thus favouring the formation of the latter phase. The positions of the boundaries are related directly to the period of the long-period superlattice and we have investigated their dependence on the electron/atom ratio and pressure. We find that the results are in very good agreement with previous experimental measurements of the average domain size in CuAu II. Thus, we provide strong evidence that Fermi surface topology plays an important role in determining the period of the long-period superlattice in CuAu II.

1. Introduction

A number of noble metal alloys form long-period superlattices (LPSs) over specific ranges of composition and temperature [1]. The two systems that have received the most attention—particularly experimentally—are **Ag**–Mg alloys near the 3:1 stoichiometric ratio and Cu–Au alloys near the equi-atomic composition. Equi-atomic CuAu has a disordered fcc structure at high temperatures but on cooling it orders, at about 410 °C, and the CuAu II phase—a one-dimensional LPS—is formed [2]. On further cooling a transformation occurs at about 380 °C to the CuAu I phase, which has the $L1_0$, layered tetragonal structure with a c/a ratio of ∼0.925. The CuAu II phase (or LPS) is composed of domains, made up of a number of 'cells' of the $L1_0$ structure, that are bounded by anti-phase boundaries each with a displacement vector $\frac{1}{2}(\boldsymbol{b}+\boldsymbol{c})$, occurring periodically along the $\boldsymbol{a}$ direction, where $(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})$ are the fundamental translation vectors of the $L1_0$ unit cell (with $|\boldsymbol{a}| = |\boldsymbol{b}|$). X-ray [2] and electron [3] diffraction studies indicate that at the equi-atomic composition there are five cells in each domain, and so the unit cell is orthorhombic with fundamental translation vectors $\sim(10\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})$. The parameter that is most often used to describe such LPSs is the average domain size, $\overline{M}$, i.e. the average number of cells per domain, which is therefore approximately five in CuAu II. However, when CuAu II is alloyed with other elements, the value of $\overline{M}$ ranges from about 1.5 to six [1, 3], and with pressure $\overline{M}$ increases at the rate of $\sim$ 1% kbar^{-1}, up to at least 50 kbar [4].

Some while ago it was suggested that the stability and detailed structure of the LPSs in Ag–Mg and Cu–Au alloys are related to the shape and size of their Fermi surfaces [1, 3, 5–7], Most of these approaches were based on free-electron models [1, 3, 5, 6] but they provided a fair indication that the Fermi surface was indeed an important factor, even

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though the surfaces of Ag_3Mg and CuAu I are certainly not free-electron-like. There is now much more convincing evidence that Fermi surface topology is the controlling factor for the LPS in **Ag**–Mg alloys, based on studies of the *proper* Fermi surfaces in both the ordered [8] and the disordered phases [9, 10]. In particular, we have shown [8] that the simplest of the LPSs in **Ag**–Mg alloys, the DO_{23} structure with $\overline{M} = 2$, is more stable than the $L1_2$ structure because the superzone boundaries that are created when the LPS is formed destroy extensive regions of Fermi surface parallel to the ΓX direction and the concomitant lowering of the electronic energy stabilizes the LPS. We showed further, using a rigid-band model, that such an approach could account for the variation of the LPS period with Mg concentration that is observed experimentally. More recently we have also provided strong evidence that the short-range order in α-phase **Ag**–Mg alloys, which, in the range ∼20–28% Mg, is a precursor to the development of the ordered LPS structures [10], is also Fermi surface driven [9].

The situation for CuAu II is a little different, however. Whereas in Ag–Mg alloys the LPS is stable to the lowest temperatures, CuAu II is a high-temperature phase and thermodynamical factors have to be taken into account in order to explain its stability relative to the CuAu I and disordered phases [3, 7, 11, 12]. The earliest, most detailed investigation was by Tachiki and Teramoto [7] who considered an expression for the free energy that included the repulsive interaction between ion cores, the contribution from the conduction electrons, the energy associated with the crystal deformation and the entropy. They argued that, because of the different temperature dependences of the various terms, the CuAu II phase becomes stabilized at high temperatures and, by using the results of an earlier electronic structure calculation for Cu, they suggested that the shape of the Fermi surface, in particular, stabilizes the LPS and determines its period. Such an explanation is consistent with our conclusions that Fermi surface topology is the underlying driving force for the LPSs in Ag–Mg alloys [8–10].

More recently, Chakraborty and Xi [12] constructed a Landau free-energy functional with which to describe the *disordered structure* → *modulated structure* → *ordered structure* transitions in equi-atomic CuAu. This functional allowed for the possibility of lattice distortions and included electronic structure effects at the level of effective medium theory (EMT). There is, however, no influence of the Fermi surface in this approach—the EMT misses such details of the electronic structure by effectively averaging out the precise electronic eigenvalue spectrum. Chakraborty and Xi [12] argued that the formation of the CuAu II phase is a consequence of the 'sizes' of the atoms and of 'electrostatic' energies, leading to a model with competing interactions reminiscent of ANNNI models [13, 14]. This model gave a reasonable account of the period of the modulation in CuAu II, but it was difficult to identify a clear reason for the stability of a five-cell structure in particular—it arose simply as a balance between two competing energy contributions—and no investigation was made of the dependence of the domain size on alloying or pressure. Thus, there appear to be two alternative mechanisms that could lead to the long-period superlattice in CuAu.

There is strong evidence that electrons at the Fermi level *must* play some role in stabilizing the LPS in CuAu II. For instance, previous experimental investigations have shown that (i) the period of the LPS is dependent on the electron/atom (e/a) ratio when CuAu II is alloyed with other elements [3], and (ii) the electronic specific heat coefficient of CuAu II is somewhat smaller than that in CuAu I [15], which is also consistent with the calculated densities of states of the two phases [16, 17]. However, the topology of the Fermi surface of CuAu I is not known and so in order to investigate what role the Fermi surface plays in stabilizing the LPS in CuAu II and in determining the dependence of the

period on alloying [1, 3] and pressure [4], it is necessary that we study the appropriate, realistic surface. Our motivation for investigating the Fermi surface of the CuAu I phase is twofold. First, as we described above, Tachiki and Teramoto [7] suggested that electronic energy differences arising from Fermi surface effects favour the CuAu II phase over the CuAu I phase. This needs to be checked using modern electronic structure calculations on the CuAu system itself, rather than pure Cu. Second, since CuAu I is tetragonal, such an investigation may provide a way of determining uniquely the modulation vector of the LPS relative to the $\boldsymbol{c}$ direction. (In contrast, Chakraborty and Xi [12] assumed that it was orthogonal to the $\boldsymbol{c}$ direction.)

In this paper therefore we describe an investigation of the Fermi surface in ordered CuAu I. We have already reported [18] some preliminary results using calculations based on the linearized, muffin-tin orbital (LMTO) method; however, here, we describe those results more fully, particularly in the light of the recent work of Chakraborty [12, 13], and we include additional calculations using the fully relativistic, Korringa–Kohn–Rostoker (RKKR) method. We find that the superzone boundaries that appear when the CuAu II phase is formed do so where there are straight and parallel regions of Fermi surface of the CuAu I phase over some distance in the ΓZ direction. We conjecture that the gaps that appear at E_F when the LPS is formed lower the total energy, thus stabilizing the CuAu II phase. We find that the variations of the average domain size, $\overline{M}$, which is determined by the positions of these straight and parallel regions, with e/a ratio and with pressure are in very good agreement with the experimental results. Furthermore, we find the topology of the Fermi surface is such that the modulation direction is orthogonal to the $\boldsymbol{c}$ direction, as observed experimentally.

2. Calculations of the fermi surface

We calculated the Fermi surface of CuAu I ($L1_0$ structure) using the self-consistent field, LMTO method, within the local density and atomic sphere approximations (the SCF–LMTO–ASA) [19, 20]. In these particular calculations the core states were treated fully relativistically and were relaxed during each iteration and the spin–orbit coupling for the valence states was included variationally; further technical details can be found in [21] and [22]. We minimized the total energy assuming equal atomic sphere radii with a fixed c/a ratio of 0.9251, the experimental value [23], and with 462 $\boldsymbol{k}$-points in the irreducible wedge of the Brillouin zone. After obtaining the self-consistent charge densities we calculated the Fermi surface at the equilibrium lattice spacings, namely $a_0 = 3.99$ Å and $c_0 = 3.69$ Å, which are some 0.8% greater than the measured values at room temperature [23]. We also determined the Fermi surfaces for a range of e/a ratios between 0.98 and 1.45, assuming rigid-band behaviour, and for several pressures up to 55 kbar.

We also carried out similar calculations of the Fermi surface of CuAu I using a fully relativistic version of the KKR method (the RKKR) [24]. We took as input 'muffin-tinized' forms of the self-consistent potentials from the LMTO calculation referred to in the preceding paragraph and we used 192 $\boldsymbol{k}$-points in the irreducible wedge of the Brillouin zone. We found that the energy bands, densities of states and the Fermi surfaces determined by the LMTO and RKKR methods were essentially identical.

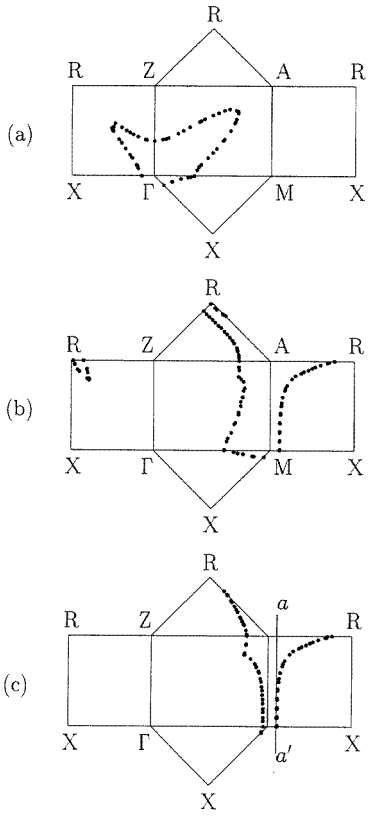

Figure 1. The Fermi surface of CuAu I determined using the LMTO method in an irreducible wedge of the tetragonal Brillouin zone. Three bands cross the Fermi energy; we show the surfaces generated (a) by the lowest band, (b) by the second band and (c) by the highest band.

3. Results and discussion

The Fermi surface of CuAu I is complicated because there are three (doubly degenerate) bands that cross the Fermi energy (E_F). For convenience we show the three surfaces generated by these bands in an unfolded wedge of the tetragonal Brillouin zone in figure 1. The surface generated by the lowest-energy band, shown in figure 1(a), bears some similarities to that obtained within the empty lattice approximation for $e/a = 1$. The other two surfaces are substantially different from free-electron surfaces. The features that are of particular interest to us here are the 'columnar' sections along the MAM direction, i.e. parallel to the $\boldsymbol{c}$ (or [001]) direction in real space. They are generated by states on the uppermost band and partially by states on the next-uppermost band, as shown in figure 1(c). The unit cell dimension along the $\boldsymbol{a}$ (or [100]) direction in CuAu II is 10 times longer than that in CuAu I and so when the former phase is formed new, superzone boundaries will be created parallel to the ΓXRZ plane and positioned at distances of $n|\mathrm{MX}|/10$ from M along MX, where n is an integer. It turns out that the distance, $\bar{x}$, from the M point to the regions labelled a–a', in figure 1(c), corresponds almost exactly to $n = 1$. The occurrence of a superzone boundary here therefore will open up a gap where there is an appreciable number of states at the Fermi energy. We suggest that this results in a contribution to

the total electronic energy which favours the formation of the CuAu II phase. In fact, the appearance of a 'pseudo-gap' at E_F is entirely consistent with the calculations of Kokko [17], who showed that the density of states at E_F is lower in CuAu II than in CuAu I, and with the observation that the experimentally measured value of the electronic specific heat coefficient in CuAu II is smaller than that in CuAu I [15].

The actual topology of the Fermi surface, and so the position where a–a' crosses the line MX will depend on the e/a ratio and the pressure. If the creation of a superzone boundary at this point is responsible for stabilizing the LPS then we can, as a result, determine the LPS modulation, i.e. the average domain size, that will produce superzone boundaries at a–a' for different e/a ratios and pressures. The relationship between the average domain size and the distance from M to where a–a' crosses the line MX, $\overline{x}$, is

$$\overline{M} = \frac{|\mathrm{MX}|}{2\overline{x}}$$

and so $\overline{M}$ can be obtained directly from the dimensions of the Fermi surface.

In order to determine $\overline{x}$ for different e/a ratios we calculated the ('new') Fermi surfaces assuming rigid-band behaviour, obtaining the shift in the Fermi energy for a change in e/a from the calculated density of states. Although $\overline{x}$ varies, it turns out that the piece of Fermi surface along a–a' remains closely parallel to AM over a fairly wide range of e/a. In figure 2 we show the calculated variation of $\overline{M}$ with the e/a ratio using both the LMTO and RKKR methods and compare them with the experimental values obtained by Sato and Toth [3] from electron diffraction patterns. The calculated sets of results are essentially identical and the agreement with the experimental values is very striking, particularly bearing in mind that there are no 'adjustable parameters' in the calculations.

We also calculated the Fermi surface of CuAu I for different pressures up to 55 kbar using the LMTO method. We find that the topology varies with pressure and we determined the corresponding values of $\overline{x}$ and $\overline{M}$. In figure 3 we compare our calculated variation of $\overline{M}$ with that obtained experimentally by Iwasaki *et al* [4] and, again, the correspondence is very good. Indeed, the agreement indicated in figures 2 and 3 strongly suggests that the structure of the LPS is governed by the topology of the Fermi surface.

4. Summary

We have investigated the topology of the Fermi surface of CuAu I and the changes with the e/a ratio and pressure. We find that the superzone boundaries that are created when the CuAu II is formed destroy appreciable regions of Fermi surface, thus favouring the latter phase. The positions of the new boundaries are related directly to the period of the LPS (i.e. the domain size) and we have shown that the experimentally observed variations of the domain size with both the e/a ratio and pressure are well reproduced by our calculations. Also, the topology of the Fermi surface is such that the modulation can only occur parallel to the $\boldsymbol{a}$ (or $\boldsymbol{b}$) directions of the CuAu I structure, in accordance with the experimental observations. Thus, we provide strong evidence that the topology of the Fermi surface plays an important role in stabilizing and determining the modulation of the LPS in CuAu II. Although the EMT approach adopted by Chakraborty and Xi [12] has been shown to reproduce the gross features of the Cu–Au phase diagram in the equi-atomic region, it cannot describe subtle Fermi surface effects [13]. We conjecture therefore that a complete description of the phase stability and structure of equi-atomic CuAu, and, in particular, the modulated structure of CuAu II, will require the construction of an improved Landau functional that contains details of the electronic structure.

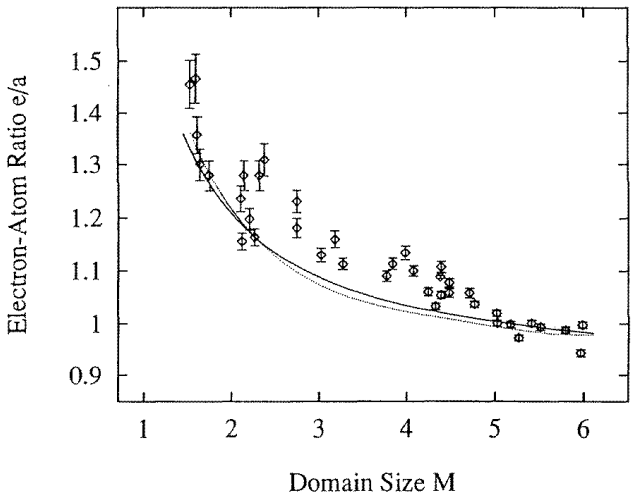

Figure 2. A comparison of the calculated and experimentally measured variation of $\overline{M}$ with e/a ratio using results from the RKKR (solid line) and the LMTO (dotted line) methods, and [3] (diamonds).

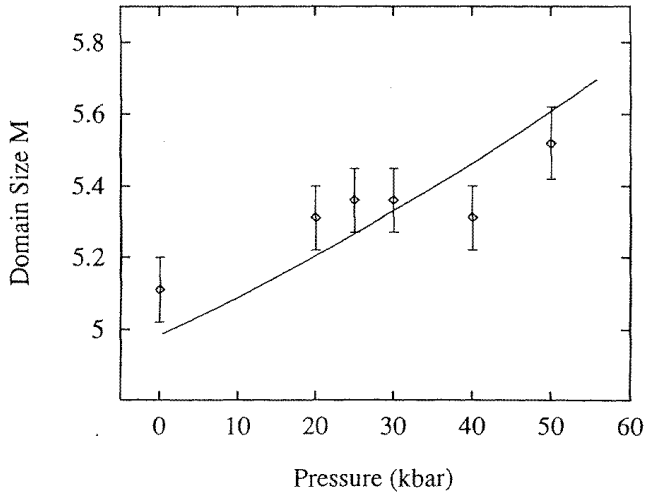

Figure 3. A comparison of the calculated and experimentally measured variation of $\overline{M}$ with pressure using results from the LMTO method (solid line) and [4] (diamonds).

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References

[1] Sato H and Toth R S 1965 *Alloying Behavior and Effects in Concentrated Solid Solutions, Metall. Soc. Conf.* vol 29, ed T B Massalski (New York: Gordon and Breach) p 295
[2] Johansson C H and Linde J O 1936 *Ann. Phys., Lpz* **25** 1
[3] Sato H and Toth R S *Phys. Rev.* **124** 1833
[4] Iwasaki H, Yosida H and Ogawa S 1974 *J. Phys. Soc. Japan.* **36** 1037
[5] Sato H and Toth R S 1962 *Phys. Rev. Lett.* **8** 239
[6] Sato H and Toth R S 1962 *Phys. Rev.* **127** 469
[7] Tachiki M and Teramoto K 1966 *J. Phys. Chem. Solids* **27** 335
[8] Jordan R G, Liu Yan, Qiu S L, Xu Xumou, Durham P J and Guo G Y 1993 *Phys. Rev.* **47** 16 521
[9] Jordan R G, Liu Yan, Qiu S L, Stocks G M, Shelton W A and Ginatempo B 1994 *Acta Metall. Mater.* **42** 3535
[10] Jordan R G 1994 *Alloy Modeling and Design* ed G M Stocks and P E A Turchi (Pittsburgh, PA: TMS) p 49
[11] See the conclusions in Ceder G, de Graef M, Delaey L, Kulik J and Fontaine D 1989 *Phys. Rev.* B **39** 381
[12] Chakraborty B and Xi Z 1992 *Phys. Rev. Lett.* **68** 2039
[13] Chakraborty B 1994 *Metallic Alloys: Experimental and Theoretical Perspectives* ed J S Faulkner and R G Jordan (Dordrecht: Kluwer) p 241
[14] Selke W 1987 *Alloy Phase Stability (NATO ASI Series E: Applied Sciences 163)* ed G M Stocks and A Gonis (Dordrecht: Kluwer) p 205
[15] Martin D L and Waterhouse N 1970 *Can. J. Phys.* **48** 1217
[16] Kokko K, Ojala E and Mansikka K 1990 *J. Phys.: Condens. Matter* **2** 4587
[17] Kokko K 1990 *J. Phys.: Condens. Matter* **2** 5253
[18] Xu Xumou, Jordan R G and Qiu S L 1994 *Metallic Alloys: Experimental and Theoretical Perspectives (NATO ASI Series E: Applied Sciences 256)* ed J S Faulkner and R G Jordan (Dordrecht: Kluwer) p 233
[19] Andersen O K 1975 *Phys. Rev.* B **12** 3060
[20] Skriver H L 1984 *The LMTO Method* (Berlin: Springer)
[21] Temmerman W M, Sterne P A, Guo G Y and Szotek Z 1989 *Mol. Simul.* **4** 153
[22] Temmerman W M and Sterne P A 1990 *J. Phys. Condens. Matter* **2** 5529
[23] Pearson W B 1958 *A Handbook of Lattice Spacings and Structure of Metals and Alloys* (Oxford: Pergamon)
[24] Guo G Y and Temmerman W M 1992 *Mater. Res. Soc. Symp. Proc.* vol 253 (Pittsburgh, PA: Materials Research Society) p 317