Electronic structure and long-period states in Ag$_3$Mg: comparison with Cu-Au alloys

Electronic structure and long-period states in Ag_3Mg: comparison with Cu–Au alloys

O I Velikokhatnyi†, S V Eremeev†‡, I I Naumov† and A I Potekaev‡

† Institute of Strength Physics and Materials Science, 634021, Tomsk, Russia
‡ Siberian Physico-Technical Institute, 634050, Tomsk, Russia

Abstract. On the basis of *ab initio* calculations of the electronic structure, an attempt is made to identify the reasons for the qualitatively different behaviours of long-period superstructures (LPS) with large and small superperiods $2M$ in alloys of noble metals. To this end, analysis is performed of the relationship between the nesting properties of the Fermi surface and the structure of LPS (of relatively small $2M$) formed in the Ag_3Mg alloy. The results of the analysis are compared with those obtained earlier for Cu–Au alloys (where LPS possess longer $2M$). It is shown that the dependence of the type of LPS on the value of $2M$ is controlled by the quality of nesting on the Fermi surface and the sensitivity of the nesting vector $2\vec{k}_F$ to variations in the long-range order parameter.

It is well known that the alloys based on noble metals, like $CuAu$, Cu_3Au, Au_3Cu, Cu_3Pd, Cu_3Pt, Ag_3Mg, and Au_3Mn, exhibit anomalous ordered phases—long-period superstructures (LPS) or superlattices (see, e.g., [1–7]). In one-dimensional LPS (it is this kind of LPS that occurs for the most part) the long period is directed along [100]. Its value is specified by the linear density of antiphase boundaries (APB), i.e., two-dimensional or quasi-two-dimensional flat defects responsible for the change in the sign of the state of the long-range order parameter describing the transition from a disordered solution to short-period superstructures $L1_0$ and $L1_2$ (the latter are known as the basic structures). The value of $2M$ expressed in terms of the length of a unit cell of the basic superstructure generally lies within the range 3–30.

A great number of experiments testify that the character and behaviour of LPS do significantly depend on the period $2M$ (see the review [7]). The LPS with comparatively long periods $2M$ are characterized by a random APB spacing (antiphase domains of varying length are stochastically distributed along the [100] direction). Their half-period M averaged over a random ensemble varies continuously with composition, taking on, among others, irrational values. These LPS are said to be incommensurate; they are formed, for instance, in Cu–Au alloys. Typically, incommensurate LPS phases are stable only in the temperature range bounded above by a symmetrical (disordered) phase and below by a low-symmetry short-period ordered structure ($L1_0$ or $L1_2$).

LPS with comparatively short $2M$ periods are generally commensurate; they occur in such alloys as Ag–Mg, Cu_3Al, and Al_3Ti. The commensurate LPS are a strictly regular (ordered) mixture of antiphase boundaries of varying length such that the average period $2M$ of the domains is invariably expressed as a rational fraction m/n (where m and n are integers). In an Ag–Mg alloy, for instance, this period assumes the following values: 10/6, 7/4, 32/18, 18/10, 26/14, and 4/2 [8]. As the alloy composition is varied, the values of m/n change

in a discrete manner and a 'devil's staircase' of commensurate transitions results. As the temperature is varied, m/n changes discretely or remains constant. As the temperature is decreased the commensurate LPS, unlike the incommensurate structures, would generally be stable and suffer no transformations.

According to concepts from [9–16], LPS appear due to the Peierls instability of the electron spectrum $\varepsilon_\lambda(\vec{k})$ resulting from the presence of flat (nesting) patches on the Fermi surface (FS) separated by the vector $2\vec{k}_F$. Disappearance of this instability is accompanied by the formation of LPS with the period $2M = 2\pi/2|\vec{k}_F|$ and by the opening of a gap on the nesting patches of the FS. It would appear reasonable to assume that characteristics of the LPS formed are controlled by the 'quality' of nesting on the parent FS, on the one hand, and by the sensitivity of the vector $2\vec{k}_F$ to variations in intrinsic and extrinsic parameters, on the other; the objective of this paper is to test the validity of this assumption. To this end, we will examine in detail the electronic structure and geometry of the FS in the Ag_3Mg system, where, as mentioned above, LPS with relatively small periods $2M$ are observed. Further, features of the spectrum $\varepsilon_\lambda(\vec{k})$ of this system will be compared against those of Cu–Au exhibiting LPS with reasonably long $2M$.

It is emphasized in [15, 16] that the structure of the LPS should, strictly speaking, be derived from the nesting features of the FS of the short-period superstructures $L1_0$ and $L1_2$, but not in a disordered alloy. This is related to the fact that the nesting vectors $2\vec{k}_F$ (small as they are) may change considerably in response to the ordering. With this in mind, the structure of the LPS will be derived for a Ag_3Mg alloy following the procedure from [15, 16] based on the electron spectrum $\varepsilon_\lambda(\vec{k})$ of an ordered state (of the $L1_2$ type).

The calculations made use of the full-potential LMTO method and the local electron-density approximation [17]. The exchange–correlation potential was taken from [18]. Integration over occupied states was performed by the tetrahedron method [19], with 165 reference points used in calculating the spectrum $\varepsilon_\lambda(\vec{k})$ and 1771 points in the irreducible part of the Brillouin zone in calculating $\chi(\vec{q})$. The lattice parameter was taken to be 7.766 au.

Figure 1 shows the electron energy spectrum $\varepsilon_\lambda(\vec{k})$ calculated for a hypothetical ordered alloy Ag_3Mg of the $L1_2$ type. A feature of this alloy, and probably of all the alloys based on
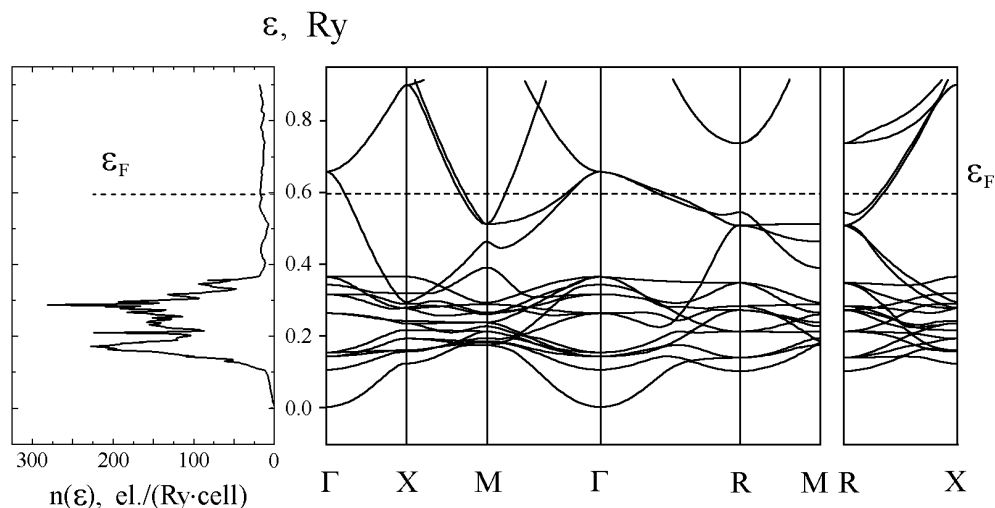

Figure 1. The electronic band structure $\varepsilon_{\vec{k}}$ and density of states $n(\varepsilon)$ for the $L1_2$ structure of Ag_3Mg.

noble metals, is a d band from Ag localized below the Fermi level, with the result that the FS is determined by the 17th, 18th, and 19th zones which are almost entirely the s and p states of Ag and Mg. It is these zones that were taken into account in calculating the electron polarizability $\chi(\vec{q})$, since they control the latter's behaviour.

Figure 2 shows the polarizability $\chi(\vec{q})$ of the Ag$_3$Mg alloy ordered as L1$_2$. It was calculated along the Γ–X direction of the Brillouin zone (with Γ–X corresponding to the period direction along which the long-period structure is formed). It exhibits a sharp maximum at the wave vector $\vec{q}_n = (2\pi/a)[0.284, 0, 0]$, which points to the instability of the hypothetical L1$_2$ phase against the formation of LPS with the period $2M = 2\pi/|\vec{q}_n| = 3.52$ (in units of a). This agrees with the experimental data. Actually, the Ag$_3$Mg system has never been observed in the L1$_2$ structure. It immediately changes from a disordered state to a long-period structure characterized by a combination of domains ordered as D0$_{22}$ ($2M = 2$) or D0$_{23}$ ($2M = 4$). The elements of the D0$_{23}$ superstructure occur more often, so the average antiphase domain period $2M$ is 3.5 [20], the above-mentioned calculated value of $2M = 3.52$ being a perfect match.
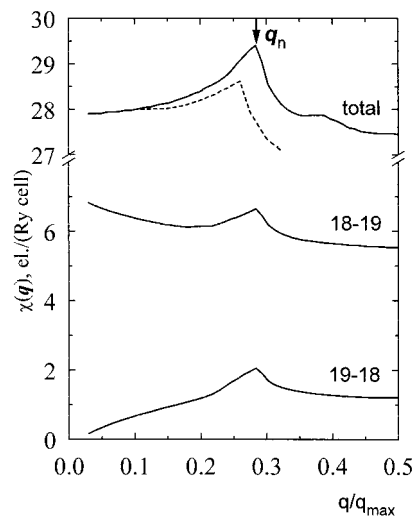

Figure 2. The electronic polarizability $\chi(\vec{q})$ and its partial contributions for Ag$_3$Mg in the $\langle 100 \rangle$ direction. The dashed curve corresponds to pure silver.

Analysis of the partial contributions to the overall polarizability $\chi(\vec{q})$ shows that its maximum is due to the electron transitions between zones 18–19 and 19–18 (figure 2). Ultimately, this maximum will be determined by the geometric characteristics of the FS displayed in figure 3. In the vicinity of point M in the Brillouin zone, there are two reasonably large electron subzones of the 18th and 19th zones of the FS which virtually coincide in their form and are separated by the vector $\vec{q}_n = (2\pi/a)[0.284, 0, 0]$.

To estimate the dependence of the long transition on the composition of the Ag$_{1-x}$Mg$_x$ alloy, let us use the 'rigid-zone' approximation. Within this approximation, the FS shape change as a function of composition x is controlled by the associated position of the Fermi level (F), or by the total number of electrons per cell $Z(x)$. Considering the fact that the valence of Ag is 1 and that of Mg is 2, we arrive at the following dependence for the total number of electrons: $Z(x) = 30 + 4((1 - x) + 2x)$, where 30 d electrons of Ag are taken into consideration. Taking the energy bands $\varepsilon_\lambda(\vec{k})$ of the Ag$_3$Mg alloy to be 'rigid', we can readily calculate the antiphase domain M as a function of composition. It is evident
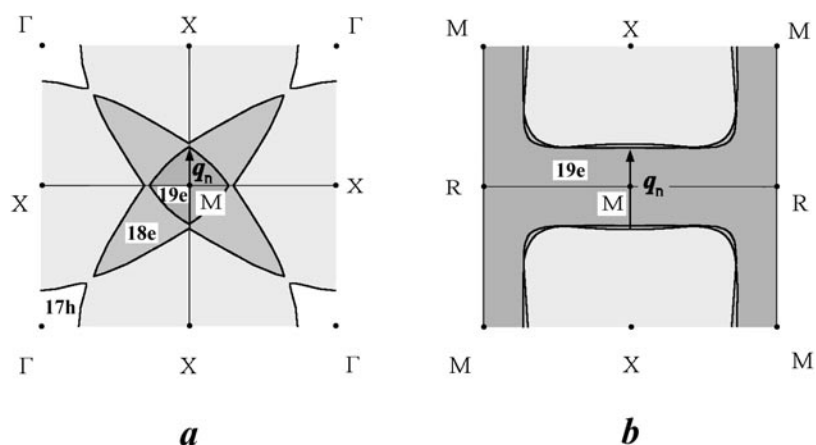
Figure 3. Fragments of the cross sections of the Fermi surface for Ag_3Mg in the plane (a) $z = 0$; (b) $z = 0.5(2\pi/a)$.

from figure 4 that the calculated curve is in good qualitative and quantitative agreement with experiment [20–22]. It is particularly remarkable that the curves are in close agreement in the vicinity of the stoichiometric composition for which the electron spectrum $\varepsilon_\lambda(\vec{k})$ was calculated. As expected, the greater the deviation from the stoichiometric composition, the rougher the rigid-zone approximation, and the greater the difference between the calculated and experimental values of M.
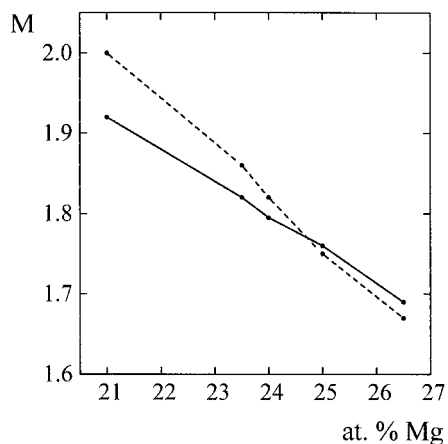

Figure 4. The dependence of the value of the long period on the composition calculated within the 'rigid'-zone approximation (solid line). The dashed line corresponds to experimental data [20–22].

As indicated earlier [15, 16], the nesting vectors $2\vec{k}_F$ (small as they are) in Cu–Au alloys tend to vary significantly with the long-range order parameter η describing phase transitions to the short-period basic structures. This brings up a question: to what extent is this effect operative in Ag_3Mg? To assess this effect let us assume the FS of the disordered Ag_3Mg alloy to be close to that of pure silver, where the Fermi level is shifted so that the electron density of s and p electrons is as high as in Ag_3Mg ($e/a = 1.25$). This is obvious from figure 5, which shows fragments of the electron spectra of Ag_3Mg and pure Ag near the
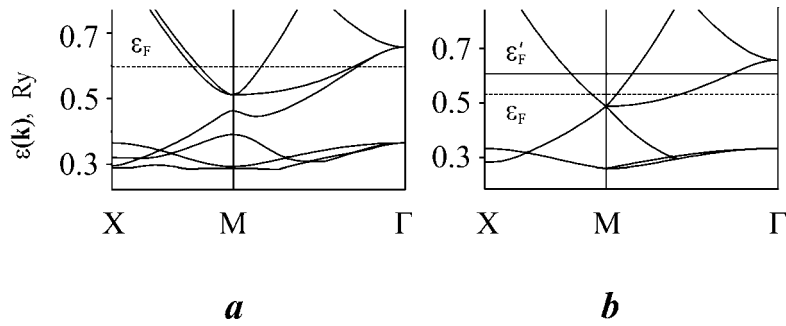
Figure 5. The electron energy spectrum $\varepsilon_{\vec{k}}$ in the vicinity of point M for Ag₃Mg (a) and Ag (b); ε'_F corresponds to $e/a = 1.25$.

Fermi level in the vicinity of point M in the Brillouin zone. The structure of Ag was taken to be formally coinciding with the L1$_2$ structure (the Fermi level for Ag corresponding to $e/a = 1.25$ is shown by a solid line). In such hypothetical Ag the susceptibility $\chi(\vec{q})$ along the $\langle 100 \rangle$ direction exhibits a pronounced peak at $\vec{q} \approx (2\pi/a)[0.26, 0, 0]$ (figure 1) which is quite close to the above-mentioned $\vec{q}_n = (2\pi/a)[0.284, 0, 0]$. Thus, a fractional change in the critical diameters of the Fermi surface $2\vec{k}_F = 2\vec{q}_n$ due to the ordering is comparatively small in Ag₃Mg as compared to Cu–Au alloys; this is obviously determined by the moduli of the vectors which are noticeably larger in Ag₃Mg than in Cu–Au.

The difference considered above dictates varying behaviours of LPS in the alloys under study depending on the order parameter η (temperature). For Cu–Au we observe a strong dependence of the length of the antiphase domain M on η [7], while this is not found for Ag₃Mg. As far as the dependence of M on the alloy composition is concerned, for Cu–Au it is still controlled by the order of η (through the character of the electron spectrum splitting) [15, 16], and for Ag₃Mg by variation of the electron density e/a and the moduli of the vectors $2\vec{k}_F$.

Another distinguishing feature of the two systems under study is as follows. In Cu–Au alloys (especially the ordered ones) the quality of nesting on the FS is rather poor, i.e., instead of a peak in $\chi(\vec{q})$ we observe, in the best case, a break of the curve [15, 16]. In the Ag₃Mg alloy, the degree of overlapping of the flattened FS is far higher, and a reasonably sharp maximum of $\chi(\vec{q})$ is observed. We believe that this difference also accounts for the stability variation of LPS as the temperature is further decreased. As the long-range order is increased in Cu–Au the nesting properties of the FS are impaired, and the tendency of the energy to foster long-period formation declines. This circumstance might be the key to understanding the reason for the LPS in Cu–Au occurring only in a narrow temperature range and tending to be energetically unfavourable as compared to the short-period structures L1$_0$ or L1$_2$ at sufficiently low temperatures. No degradation of nesting is observed in Ag₃Mg, and the LPS maintain their stability down to low temperatures [7].

The degree of overlapping of the FS is another critical factor affecting the commensurability of the resulting LPS. We might expect that systems with a high-quality nesting (such as Ag₃Mg) will give rise to commensurate LPS due to strong 'anharmonic' interaction of the incommensurate concentration waves with the periodic potential of the parent phase [14]. And vice versa, in systems with a weak feature at $\chi(\vec{q})$ (such as Cu–Au), incommensurate LPS are expected to form. This argument is strongly supported by the Cu–Pd system in which the 'commensurability–incommensurability' transition (lock-in transition) occurs along the axis of the Pd content (21.3 at.% of Pd) [5]. On the basis of the above speculation, we might expect a decrease in the curvature of the critical FS patches with increase in the Pd content. Indeed,

self-consistent *ab initio* FS calculations for the Cu–Pd alloys using the KKR-CPA method [24] revealed an increase in the flattening of the FS patches along $\langle 110 \rangle$ with increase in the Pd concentration.

Thus, the critical FS diameter $2\vec{k}_F$ in Ag–Mg alloys is found to increase compared to that for Cu–Au alloys, while the period $2M$ in the LPS is diminished. Also, in Ag–Mg alloys the nesting on the FS is improved, and the feature at $\chi(\vec{q})$ is more pronounced (a sharp maximum is observed instead of a break in the curve). These changes in the electron structure lead to: (1) disappearance of dependence of the long-period TM on the ordering η or temperature, (2) a wider temperature range of the LPS stability, and (3) transition of the LPS from incommensurate to commensurate structures.

The fact that the change in the FS nesting properties with varying η in Ag_3Mg is negligible is supported by analysis of the stability of the LPS developing in the alloy based on the spectrum of the disordered state; this approach has been used in earlier works (e.g. [10–14, 23]).

Acknowledgments

References

[1] Sato H 1952 *Sci. Rep.; Res. Inst. Tohoku Univ.* **1** 169
[2] Guymont M and Gratias D 1976 *Phys. Status Solidi* a **36** 329
[3] Watanabe D 1979 *Int. Conf. on Modulated Structures (Kailua Kona, Hawaii, 1979)* (New York: Elsevier) p 229
[4] Matveeva N M and Kozlov E V 1989 *Ordered Phases in Metal Systems* (Moscow: Nauka) p 247 (in Russian)
[5] Broddin D *et al* 1986 *Phil. Mag.* **54** 395
[6] Watanabe D and Terasaki O 1984 *Symp. on Phase Transformation in Solids (Maleme-Chania, Crete, 1983)* (New York: Elsevier) p 231
[7] Potekaev A I 1995 *Izv. Vyssh. Uchebn. Zaved. Fiz.* **6** 3
[8] Guymont M, Gratias D and Portier R 1979 *Int. Conf. on Modulated Structures (Kailua Kona, Hawaii, 1979)* (New York: Elsevier) p 244
[9] Dement'ev V M and Kozlov E V 1973 *Izv. Vyssh. Uchebn. Zaved. Fiz.* **6** 21
[10] Dement'ev V M and Kozlov E V 1974 *Izv. Vyssh. Uchebn. Zaved. Fiz.* **6** 30
[11] Wul' D A and Krivoglaz M A 1981 *Fiz. Met. Metalloved.* **51** 231
[12] Wul' D A and Krivoglaz M A 1983 *Fiz. Met. Metalloved.* **55** 869
[13] Krivoglaz M A 1983 *Zh. Eksp. Teor. Fiz.* **84** 355
[14] Krivoglaz M A 1984 *Diffuse Scattering of X-rays and Neutrons by Fluctuating Inhomogeneities in Non-Ideal Crystals* (Kiev: Naukova Dumka) p 287 (in Russian)
[15] Velikokhatnyi O I, Eremeev S V, Naumov I I and Potekaev A I 1999 *JETP Lett.* **69** 589
[16] Velikokhatnyi O I, Eremeev S V, Naumov I I and Potekaev A I 2000 *JETP* **90** 421
[17] Savrasov S Yu and Savrasov D Yu 1992 *Phys. Rev.* B **46** 12 181
[18] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
[19] Rath J and Freeman A J 1975 *Phys. Rev.* B **11** 2109
[20] Guymont M and Gratias D 1979 *Acta Crystallogr.* A **35** 181
[21] Sato H, Fujino Y, Hirabayashi M and Koyama Y 1988 *Int. Symp. on Dynamic Ordering Processes in Condensed Matter (Kyoto, Japan, 1987)* (New York: London) p 519
[22] Fujino Y, Sato H and Hirabayashi M 1988 *Proc. Conf. on Phase Transformations in Metals (Scientific Communications of the Institute of Metals) (Cambridge, UK, 1987)* (London: Institute of Metals) p 585
[23] Tashiki M and Teramoto K 1966 *J. Phys. Chem. Solids* **28** 375
[24] Gyorffy B L and Stocks G M 1983 *Phys. Rev. Lett.* **50** 374