Origin of long-period superlattices in Ag-Mg alloys

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(Received 14 January 1993)

We have calculated the electronic structures and the relative stabilities of Ag_3Mg, assuming the $L1_2$, DO_{22}, and DO_{23} structures. We provide strong evidence that the formation of the DO_{23} structure in particular, and other long-period superlattices in general around the 3:1 stoichiometry, is driven by the topology of the Fermi surface.

I. INTRODUCTION

It has been known for some time that a number of noble-metal alloys form long period superlattices (LPS's) over definite ranges of composition.[1] The two systems that have received the most attention are near equiatomic Cu-Au alloys and Ag-Mg alloys around the 3:1 stoichiometric composition. In the latter case, the alloys have the disordered fcc structure above about 400 °C, but on cooling they undergo a transformation to an ordered α' phase.[2] This ordered phase is a one-dimensional LPS (Ref. 3) whose actual structure depends on thermal history and composition. A multitude of different LPS's have been identified in Ag-Mg alloys using, predominantly, high-resolution transmission electron microscopy; see, for example, Refs. 4–7 and references therein. These LPS's are comprised of domains, based on the $L1_2$ structure, bounded by antiphase boundaries (APB's), each with a displacement vector $\frac{1}{2}(\mathbf{a}+\mathbf{b})$, where **a**,**b**,**c** are the fundamental translation vectors of the (cubic) unit cell of the $L1_2$ structure, occurring periodically along the **c** direction. The simplest of the observed LPS has the DO_{23} structure, with a c/a ratio very close to 4, which occurs at $22-23\%$ Mg.[6,7] If the two domain subunits on opposite sides of an APB are labeled + and −, then the unit cell of the $L1_2$ structure can be written as [+], or equivalently [−], and that of the DO_{23} structure as [+ + − −]. It should be noted that neither the $L1_2$ structure nor the structure with the shortest possible modulation wavelength, i.e., the DO_{22} structure or [+−], occur in the range $20-30\%$ Mg.

It has been suggested that the stability of LPS in both CuAu II and Ag_3Mg is related to the shape and size of their Fermi surfaces.[1,6,8–11] This explanation is elegant and appealing, particularly since Gyorffy and Stocks,[12] for instance, using a first-principles approach, have shown that the existence of flat, parallel sheets of Fermi surface is the underlying cause of the observed short-range order in Cu-Pd alloys. Because of (i) the dependence of the LPS periodicity on the number of "free" electrons per atom when CuAu II is alloyed with other elements[8] and (ii) the difference in the electronic specific heat coefficients of CuAu I and CuAu II,[13] which is also reflected in the calculated densities of states at the Fermi energy E_F,[14,15] it seems that for CuAu II at least there is good evidence that electrons at E_F *must* play some part in stabilizing the LPS. The original interpretation proposed by Sato and Toth[1,8–10] was based on a free-electron description. However, the fact is that the topologies of the Fermi surfaces of CuAu II and Ag_3Mg are not known, but it is to be expected that they will deviate from that for free electrons. Consequently, it is not clear precisely what role the Fermi surface plays in stabilizing the LPS in these alloys.

In the study reported here we focus our attention on the formation of LPS in Ag-Mg alloys. We have calculated the electronic structures and the relative stabilities of Ag_3Mg with the $L1_2$, DO_{22}, and DO_{23} structures. We find that the DO_{23} phase has the lowest energy, which we suggest is due to the fact that the Fermi surface for the $L1_2$ structure has parallel regions at which the "nesting" of superzone boundaries can occur, with a concomitant lowering of the electronic energy. The vector connecting these parallel regions is in the [001] direction and its magnitude is consistent with the formation of a LPS with a modulation wavelength of almost exactly $4a_0$, where a_0 is the cubic unit-cell dimension of the $L1_2$ structure. To our knowledge, what we report here is the first *a priori* evidence that the Fermi-surface topology may provide the underlying driving force for the formation of LPS in Ag-Mg alloys.

II. CALCULATIONAL DETAILS

We calculated the electronic structures of Ag_3Mg with the $L1_2$, DO_{22}, and DO_{23} structures using the self-consistent-field, linearized-muffin-tin-orbital

0163-1829/93/47(24)/16521(4)/$06.00

(LMTO) method, within the atomic sphere approximation (ASA).[16,17] The LMTO-ASA method is a fast technique — at the expense of only a small loss in accuracy — and is particularly useful when used for structures with many atoms per unit cell. In our calculations we only included angular momentum components up to $\ell = 2$ in the basis functions since we expect that higher components play a negligible role. We assumed equal atomic sphere radii for Ag and Mg — in earlier studies of β'-AgMg,[18] we found that the use of different sphere sizes had an insignificant effect on results — and we used the von Barth–Hedin form for the local exchange and correlation.[19] When determining initially the equilibrium Wigner-Seitz radii we used the scalar relativistic approximation; in a final set of calculations for the relative total energies and the Fermi surface for the $L1_2$ structure, the core states were treated fully relativistically and were relaxed during the iteration process, and the spin-orbit coupling for the valence states was included variationally. Further technical details can be found in Refs. 20 and 21. In order to make proper comparisons between the different structures we used the same lattice in each case, i.e., tetragonal with $c/a = 4$, and the same distribution of **k** points in the irreducible wedge of the Brillouin zone. Thus, in the notation introduced earlier, the units cells we adopted were $[++++]$, $[+-+-]$ and $[++--]$ for the $L1_2$, DO_{22}, and DO_{23} structures, respectively, with each containing 12 Ag and 4 Mg atoms.

III. RESULTS AND DISCUSSION

In Fig. 1 we show the variations of the relative total energies of Ag_3Mg assuming the $L1_2$, DO_{22}, and DO_{23} structures with Wigner-Seitz radius. Clearly, the DO_{23} phase has the lowest energy. The equilibrium Wigner-Seitz radii for the different structures are all very similar; the corresponding values of the equilibrium lattice constants and the bulk moduli, calculated from the pressure versus volume curves, are shown in Table I. (The calculated lattice constant for the DO_{23} structure is slightly smaller than that reported from x-ray diffraction measurements at room temperature for the ordered phase at $\sim$ 25% Mg — a value of 4.11 Å is cited in several sources[22–25] — but it is very close to that obtained by extrapolating the published data of Hämäläinen, Laine, and Tarna[24] to $T = 0$.) These particular calculations were carried out within the scalar relativistic approximation with 56 **k** points in the irreducible wedge of the Brillouin zone. We subsequently carried out a further set of fully relativistic calculations for each of the structures at the corresponding equilibrium lattice constant and with an increased number of **k** points in the irreducible wedge, i.e., for 72 and 135 points. In Fig. 2 we show that, although the calculated total energy depends on the number of **k** points chosen, the variations with the inverse of the latter are closely parallel. Thus the observed relative stability of the DO_{23} structure in the calculations does not depend on the number of **k** points selected. These total energy calculations also indicate that it is not the energy associated with APB's *per se* that stabilizes the DO_{23} structure since the latter contains only half as many APB's as the DO_{22} structure. In order to understand the relative stability of the DO_{23} phase we have to consider the topology of the Fermi surface of Ag_3Mg with the $L1_2$ structure.

TABLE I. Values of the relative total energies of Ag_3Mg with the $L1_2$, DO_{22}, and DO_{23} structures, the corresponding calculated equilibrium lattice constants, and bulk moduli.

	$L1_2$	DO_{22}	DO_{23}
Total energy (mRy)	+12.5[a]	+10.1[a]	0.0
	+9.4[b]		0.0
Lattice constant (Å)	4.096	4.097	4.093
Bulk modulus (MBar)	1.12	1.12	1.14

[a]From Fig. 1.
[b]Extrapolated value from Fig. 2.

In Fig. 3 we show the Fermi surface of Ag_3Mg with the $L1_2$ structure in an unfolded wedge of the simple cubic Brillouin zone. For clarity we show separately the surfaces generated by bands 17, 18, and 19 in Figs. 3(a), 3(b), and 3(c), respectively. The surface produced by band 17 is very similar to that obtained in the empty

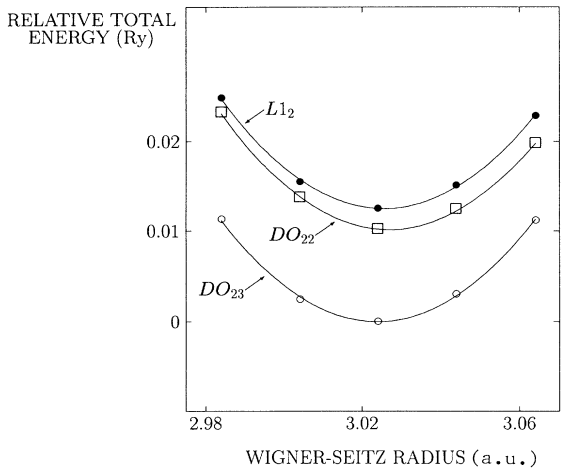

FIG. 1. The variation of the relative total energies of the $L1_2$, DO_{22}, and DO_{23} phases with Wigner-Seitz radius. Each set of data has been fitted to a parabola.

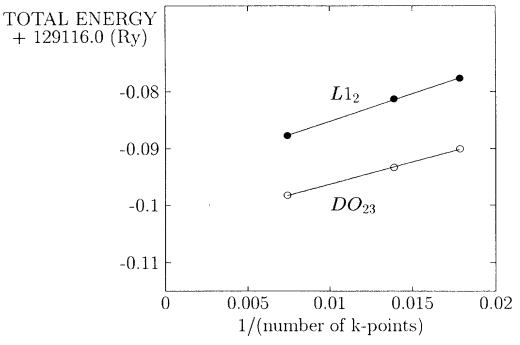

FIG. 2. The variation of the total energies of the $L1_2$ and DO_{23} structures with the inverse of the number of **k** points in the irreducible wedge of the Brillouin zone.

lattice approximation with an electron to atom ratio of 5/4, whereas the surfaces produced by bands 18 and 19 show substantial deviations from free-electron-like behavior. Of particular interest is the region labeled a–a' in the $MXMR$ plane in Fig. 3(c). This piece of Fermi surface is very closely parallel to MX and the creation of a superzone boundary here will result in a lowering of the total electronic energy. Since this section of Fermi surface crosses the line XM at a distance of very nearly $0.75|\Gamma X|$ from X, the formation of the DO_{23} phase, with a unit cell dimension of $4a_0$ in the [001] direction, produces such a boundary. We suggest that this accounts for the relative stability of the DO_{23} structure.

The actual topology of the Fermi surface and therefore the length of the vector $\mathbf{K}$ that connects the parallel regions depends on the number of electrons. If we assume a rigid band model, with each Ag(Mg) atom contributing 1(2) valence electrons, we can determine how its magnitude varies with concentration and supposing that the LPS are stabilized by the appearance of superzone boundaries at these parallel regions, we can investigate the occurrence of other LPS. In Fig. 4 we show the calculated variation of $\frac{1}{2}|\mathbf{K}|/|\Gamma X|$ with Mg concentration, where $|\mathbf{K}|$ is determined from the point of intersection along XM. Experimentally, the LPS of annealed samples tend to have the form $\langle 2^j 1\rangle$ — in our previous notation, the LPS $[++--++-]$, for example, is written $\langle 2^3 1\rangle$. The unit-cell dimension in the [001] direction for each structure is then qa_0, where

$$q = \begin{cases} 2j+1 & \text{if } j \rightarrow \text{odd} \\ 2(2j+1) & \text{if } j \rightarrow \text{even,} \end{cases}$$

and so superzone boundaries will occur at $(00p/q)$ planes in the Brillouin zone, where p is an integer $(< q)$. In Fig. 4 therefore we have also plotted values of p/q for the LPS observed by Fujino, Sato, and Otsuka[6] and Kulik, Takeda, and de Fontaine.[7] (We select these particular data because they are for annealed samples and are more likely to represent the *equilibrium* structures.) The agreement between the calculated values of the nesting vector and the observed superzone boundary positions, and their variation with Mg concentration is very good. We suggest that this provides strong evidence that the stabilization of the different LPS observed is driven by the topology of the Fermi surface. We can also understand why the $L1_2$ and DO_{22} phases do not occur; the corresponding required values of $p/q = 1$ and $p/q = \frac{1}{2}$ lie well outside the concentration range of the LPS.

Studies by Iwasaki, Yoshida, and Ogawa[26] of the LPS in CuAu II showed that the period increased by some 10% upon the application of $\sim$ 50 kbar pressure. They argued that this increase was consistent with changes in the topology of the Fermi surface with pressure. Although, to our knowledge, there have been no measurements of the pressure dependence of the LPS period in Ag-Mg alloys, we investigated this effect in Ag_3Mg by calculating the variation of $\frac{1}{2}|\mathbf{K}|/|\Gamma X|$ with pressure. The results are shown in Fig. 5. We see that even with an applied pressure of $\sim$ 100 kBar the calculated average domain size $\overline{M}$, where

$$\overline{M} = \frac{1}{2-2\kappa}$$

and $\kappa = \frac{1}{2}|\mathbf{K}|/|\Gamma X|$, only increases from $\sim$ 1.97 to

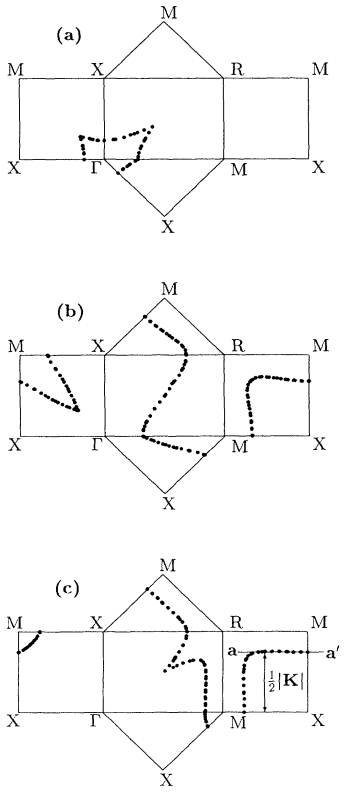

FIG. 3. The Fermi surface of Ag_3Mg with the $L1_2$ structure; (a) is for band 17, (b) is for band 18, and (c) is for band 19.

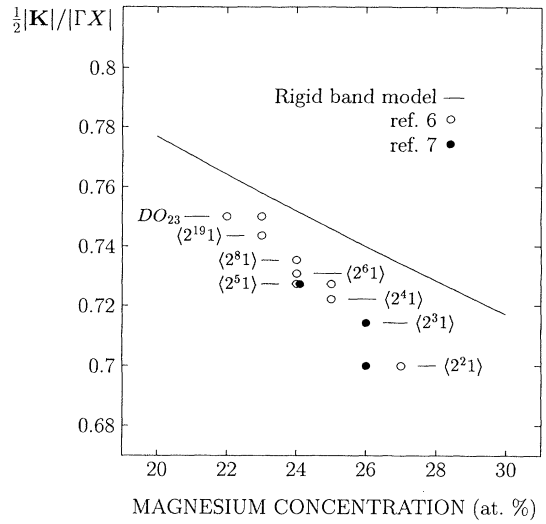

FIG. 4. The variation of $\frac{1}{2}|\mathbf{K}|/|\Gamma X|$, assuming a rigid band model, with Mg concentration and values of p/q for the experimentally observed LPS from Refs. 6 and 7.

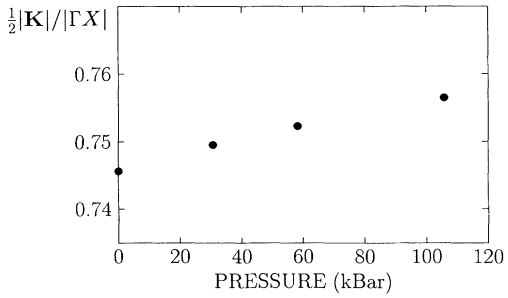

FIG. 5. The calculated variation of $\frac{1}{2}|\mathbf{K}|/|\Gamma X|$ with pressure.

~ 2.05. Clearly, this is much smaller than the change observed for the LPS in CuAu II.

IV. SUMMARY

Summarizing, therefore, in this paper we provide strong evidence that the LPS in Ag-Mg alloys near the 3:1 composition are stabilized by the presence of superzone boundaries at parallel regions of Fermi surface of the $L1_2$ structure. In addition, using a rigid band model we have shown that a range of different LPS can be produced by varying the Mg concentration, as observed experimentally. Furthermore, assuming that Fermi-surface topology is the driving force for the occurrence of LPS, our calculations indicate that the average domain size is not strongly dependent on pressure. We are currently carrying out similar investigations of the LPS in CuAu II.

ACKNOWLEDGMENTS

This work was supported in part with funds granted by the NSF (DMR-9120120) to R.G.J. and S.L.Q. R.G.J. and P.J.D. are grateful to NATO for supplying travel funds under the Collaborative Research Grants Program. The authors thank Dr. Luc Wille for discussions, Florida State University for the provision of CRAY supercomputer resources, and the United Kingdom Science and Engineering Research Council for time on the INTEL iPSC/860 parallel supercomputer at the Daresbury Laboratory.

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