Komoda: J. Phys. Soc. Japan **14** (1959) 936.

18 D. Watanabe: J. Phys. Soc. Japan **16** (1961) 469.

19 P. Perio and M. Tournarie: Acta Cryst. **12** (1959) 1044.

20 J. M. Cowley: Phys. Rev. **120** (1960) 1648.

21 D. W. Pashley and A. E. B. Presland: *Structure and Properties of Thin Films* (Proceedings of an International Conference at Botton Landing, New York, September, 1959) 199.

22 S. Ogawa and D. Watanabe: Presented at the Symposium "Direct Observation of Imperfection in Crystals" at St. Louis, March, 1961.

23 R. M. Fisher and M. J. Marcinkowski: J. Appl. Phys. **31** (1960) 1687, Phil. Mag. **6** (1961) 1385.

24 S. Yamaguchi, D. Watanabe and S. Ogawa: To be published, read at the Spring Meeting of Phys. Soc. Japan at Tokyo, April, 1961.

25 R. E. Scott: J. Appl. Phys. **31** (1960) 2112.

26 K. Schubert: Z. Metallkde. **46** (1955) 43.

27 K. Adachi: Read at Spring Meeting of Phys. Soc. Japan at Tokyo April, 1961.

28 R. S. Toth and H. Sato: Phys. Rev. **124** (1961) 1833.

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On the Long Period Superlattice in Alloys

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To investigate the origin of long period superlattices found in alloys, a detailed study of factors which affect the period of CuAu II was made. Utilizing the thin film technique, the effect of many additional elements in varying concentrations on the domain size of CuAu II was determined using electron diffraction. From the data, a definite relation was found between the electron-atom ratio of alloys and the domain size. There did not appear to be any systematic relation between the data and other factors such as atomic size, weight, etc. From these results, a theory based upon the stabilization of alloy phases at the Brillouin zone boundary was formulated to show the variation of the electron-atom ratio with the domain size. The agreement between theory and experiment is excellent. In addition, the model gives a good explanation of other one and two dimensional superlattices found in A_3B type alloys.

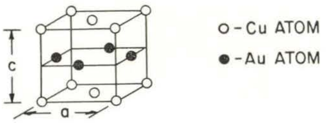
Introduction

The superlattice CuAu II is a modification of the ordered CuAu I structure and is characterized by regular antiphase boundaries at each 5 unit cell lengths in the *b*-direction. This alloy, at the stoichiometric composition CuAu, exists between the disordered phase and ordered CuAu I phase, whose transition temperatures are 410°C and 380°C respectively. The unit cells of the two ordered structures are shown in Fig. 1. Experimental data indicate that CuAu II is not a transition phase but an equilibrium phase. Consequently the question arises why the alloy prefers to take a complicated antiphase structure instead of the usual simple one. These long period structures have been found in many alloy systems,[1] and because of their frequent occurrence, their stability should be due to a common origin. This paper discusses the attempts made to understand the origin of long period superlattices, taking CuAu II as a typical example.[2]

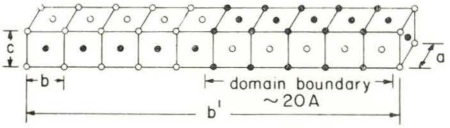
Experimental method and results

One of the characteristics of a long period superlattice is the period or domain size M, as shown in Fig. 1. To investigate the origin of such a superlattice, one should determine what factors affect the period and the stability range.

The domain size can be obtained from the



a) UNIT CELL OF CuAu I



b) UNIT CELL OF CuAu II

Fig. 1. Unit cells of the ordered phases of CuAu: (a) CuAu I, (b) CuAu II.

separation of the superlattice spots in the direction of the period in X-ray or electron diffraction patterns. Consequently, we decided to use the single crystal thin film method and to use electron diffraction to measure the period.[3] This method has an advantage over growing bulk crystals because of its ease and speed in obtaining good single crystals. The method consisted of preparing single crystal thin films of CuAu by complete successive evaporation of Au and Cu, in a vacuum of 5×10^{-5} Torr or less, onto a freshly cleaved single crystal of NaCl held at an appropriate temperature. The films were then placed in a hot stage in a RCA-EDU unit having an average accelerating voltage of 50 kv, so that information could be obtained on the various phase changes in addition to the necessary pattern of CuAu II. Figure 2 shows a typical diffraction pattern of CuAu II, in this case containing Al. The domain size M was obtained by measuring the separation of the superlattice spots relative to the (200) separation, the separation of the superlattice spots being dependent on the length of the antiphase domain. A total of 16 elements of high purity (Al, Ga, In, Sb, Bi, Mg, Fe, Ni, Pd, Cr, Zn, Ag, Sn, Ge, Be, and Mn) in varying concentrations were added to CuAu II films and their effects noted. Among them, Sb, Be, Cr, Bi and Mg do not form a solid solution in a wide enough range to investigate their effect on CuAu II. However, other elements form an extensive solid solution with the CuAu alloy and a detailed determination of the period can be done. In general, it was found that elements having more valence electrons than the matrix reduced the size of the domain. For example, Al, Ga, and In caused a systematic

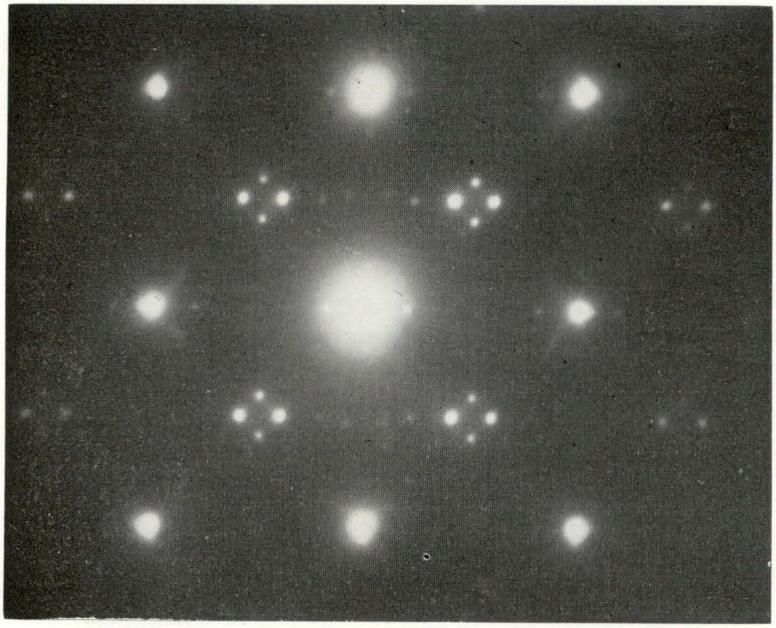


Fig. 2. Electron diffraction pattern of CuAu II containing 5.8% Al.

decrease in M to 1.5 with added concentration of the element. A typical curve is shown in Fig. 3. On the other hand, elements with less-valence electrons increased M. Information concerning the transition temperature was also obtained.

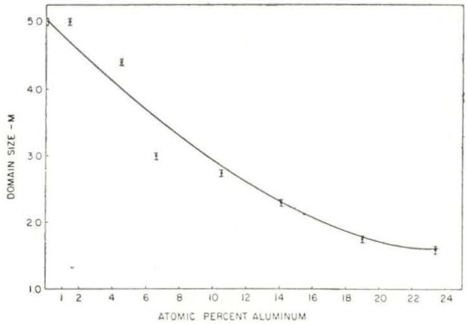


Fig. 3. Domain size M vs. concentration of Al in CuAu II.

The data was plotted in several ways to look for a dependence of the domain size on such factors as electron concentration, atomic size, atomic weight, etc. It was found that there was a systematic change in domain size with the electron-atom ratio of the alloy. This is shown in Fig. 4. The scatter of points in the curve is probably due to the evaluation of the concentration of the atomic species since they were calculated on the assumption of total evaporation of measured amounts of the materials. Apart from the dependence of M on e/a, we cound not find a regular dependence between M and the other factors. In replotting the data with e/a vs. $1/M$, an approximately linear curve is obtained which is similar to that obtained by Schubert[4)] on many alloy systems. The extrapolation of the linear curve indicates that $M=\infty$ at $e/a=0.85$, which means that CuAu I occurs. There is also a relation between the stability range and the period. In other words, as the period becomes longer, the relative stability of CuAu I increases. The addition of Au, Cu or Ag to the stoichiometric CuAu II increases the period. Since the number of free electrons is similar for all these elements, this result indicates a systematic deviation from the above relation between e/a and M.

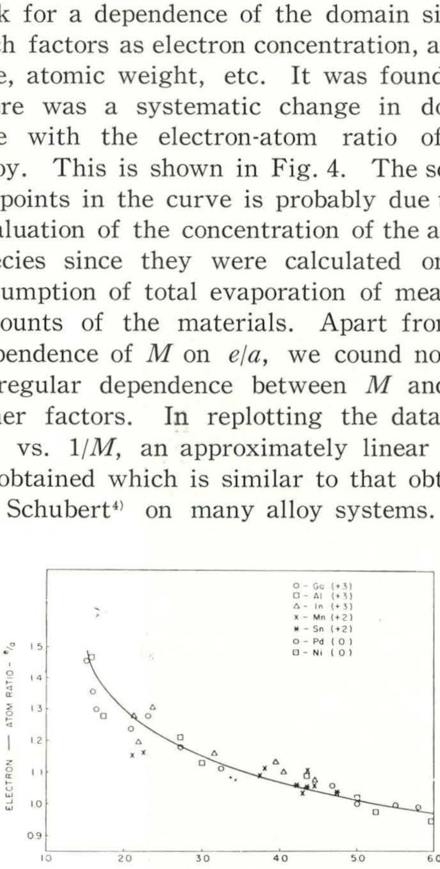


Fig. 4. Electron-atom ratio vs. domain size M using the indicated valences for the elements tested.

Theoretical interpretation

In general, long period superlattices are equilibrium phases at low temperatures, and hence should be energetically more favorable than the usual simple superlattice. Among possible mechanisms which stabilize this type of structure and which depend upon the number of free electrons as the experiment suggests, it was found that the reduction in the kinetic energy of the free electrons at the Brillouin zone boundary[5)] is responsible for the formation of these structures. Since any mechanism should cause a splitting of the Brillouin zone as a result of having an extra period, it should specifically be established that the splitting of the Brillouin zone itself is the origin of the stabilization.

The Brillouin zone structure for the disordered f. c. c. alloy is a truncated octahedron. When an AB type tetragonal

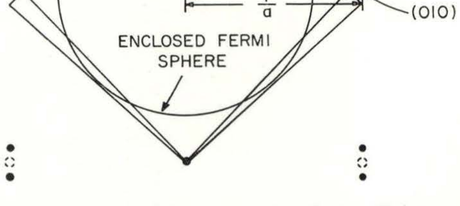


Fig. 5. Reciprocal lattice of CuAu II in a plane through the origin and parallel to the (001) plane, showing the structure of the Brillouin zone of CuAu II and of the enclosed Fermi sphere.

superlattice as CuAu I is formed, the Brillouin zone splits and the new first Brillouin zone is bounded by two {001} planes and four {110} planes. This Brillouin zone contains one electron per atom and it is found that the energy gaps at the boundaries are rather small. The Fermi surface then overlaps with the second zone rather freely in the [001] direction but should be close to the {110} surfaces and these should have an important effect on the problem. In Fig. 5, the cross section of the Brillouin zone by an (001) plane through the origin is shown. When the CuAu II superlattice is formed, the superlattice spots at the (110) positions separate in the direction of the period. Consequently, the {110} faces in the Brillouin zone also separate as shown in Fig. 5. The separation is inversely proportional to the period and the experiment indicates that the separation becomes bigger as the *e*/*a* ratio becomes bigger. Thus, it seems reasonable to assume that, as the number of electrons increase and the size of the Fermi sphere increases, the size of the Brillouin zone increases due to the splitting in such a way that the Fermi surface is always at the Brillouin zone boundary thereby maintaining the maximum stabilization. The volume of the inscribed Fermi sphere, hence the number of electrons per atom *e*/*a* included in this sphere is given by the following formula, if some correction for the non-sphericity of the electron distribution in *k*-space is taken into account:

$$e/a=(\pi/12t^3)(2\pm x+x^2)^{3/2}. \tag{1}$$

Here x is one half the separation of the (110) spot and the difference in signs applies to the outer or the inner Brillouin zone boundary. The truncation factor t accounts for the non-sphericity of the Fermi surface and is taken as an adjustable parameter to be determined from the best fit to the experimental data or from a known point. Assuming stoichiometric CuAu II where $M=5.0$ as the fixed point, a value of $t=0.95$ is found, and the comparison between theory and experiment using this value is shown in Fig. 6. The agreement is good. In addition, Eq. 1 shows that the limiting value of *e*/*a* for $M=\infty$ is 0.86 as compared to the value of 0.85 obtained by linearly extrapolating the *e*/*a* vs. $1/M$ curve. A better fit to the experimental data at larger *e*/*a* values is obtained by assuming $t=0.94$. Curve (b) in Fig. 6 represents the stabilization at the inner zone boundary. This curve gives a good explanation for the Cu-Pd alloy near Cu_3Pd.[6)]

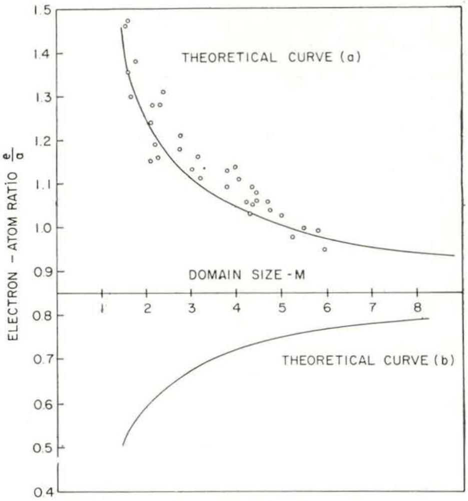


Fig. 6. Theoretical curve of e/a vs. M with $t=0.95$ for (a) stabilization by outer Brillouin zone and showing its relation to the experimental points for CuAu II, and (b) stabilization by inner zone.

When the Fermi surface is close to the Brillouin zone boundary a force is exerted such that the Brillouin zone comes closer to the Fermi surface. This results in a contraction of the Brillouin zone in the direction of the period when the stabilization occurs at the outer Brillouin zone boundary and an extension when stabilization is at the inner zone boundary. This accounts for the distortion in the lattice when a long period structure is formed and agrees well with observation. These agreements indicate that the present model is appropriate for the origin of the periodic structure.

Introduction of the antiphase boundary increases the energy of the system due to the short range interaction. The contribution of this term has the effect of increasing the period above that predicted by Eq. 1. This could explain the systematic deviation of experimental results from the theoretical curve, and in addition, account for the increase in period when either Ag and Cu or Au, above the stoichiometric proportion, is added to CuAu. Further, if the boundary energy is larger than the stabilization at the Brillouin zone boundary, the long period structure would not appear. It seems that in the Cu-Au alloy, the two energy terms are very close and hence there is a sensitive dependence of the period on the concentration of the alloy. This would also explain the appearance of CuAu I below CuAu II in the phase diagram.

For the A_3B type superlattice, the Brillouin zone to be considered is a rhombic dodecahedron and has three sets of four (110) faces instead of one set as in the AB alloy. By having an extra period in one direction, two sets of these faces are affected, but in order to obtain a better fit of the Fermi surface to all faces, a two dimensional super period is required. This indicates why two dimensional antiphase structures[6] are found in A_3B type alloys. The relation between e/a and M for one dimensional antiphase structures is also given by Eq. 1 and a good agreement is obtained for many alloys using a truncation factor $t \doteqdot 0.95$. A similar relation holds between e/a and the two periods in the two dimensional case. The relation also tells that M_1 should be somewhat different from M_2.

Another difference of the A_3B type structure from the AB type is the appearance of two types of "out of step" at the antiphase boundary of the A_3B structure.[6] It follows, from the condition of best fit of the Fermi sphere to the Brillouin zone boundary, that the "out of step" for one dimensional structures should be of the first kind. For two dimensional structures, a mixture of the first and second kind is preferred when the period is not very short.

The importance of the boundary energy indicates that the main origin of the ordering in Cu-Au and other similar alloys is due to the usual short range interaction. The Brillouin zone mechanism accounts for the small difference in energy between the ordinary type structure and the long period structure.

References

1 L. Guttman, *Solid State Physics* **3** (1956) 174.

2 The detail of this paper: H. Sato and R. S. Toth, "Effect of Additional Elements on the Period of CuAu II and the Origin of the Long Period Superlattice", Phys. Rev. **124** (1961) 1833.

3 See for example: S. Ogawa and D. Watanabe, J. Phys. Soc. Japan, **9** (1954) 435.

4 K. Schubert, B. Kiefer, M. Wilkens, and R. Haufler: Z. Metallkde. **46** (1955) 692.

5 See for example: G. V. Raynor, *Progress in Metal Physics* **1** (1949). 1.

6 D. Watanabe and S. Ogawa: J. Phys. Soc. Japan **11** (1956) 226.

DISCUSSION

S. OGAWA: If the fitting of the Fermi sphere with the Brillouin zone boundary is a necessary condition for the formation of the periodic anti-phase structure, then, why don't usual metal lattices have such Brillouin zones as filled with electrons? Can you explain the origin of the periodic anti-phase structure of 3 to 1 type lattice?

H. SATO: The appearance of the extra period on forming a long period superlattice introduces the antiphase boundaries and this causes an extra energy. The relative magnitude of this energy term and the reduction in the energy of free electrons at Brillouin zone boundaries determines whether the long period superlattice is stabilized or not. In the case of Cu-Au alloys, these two energy terms seem to be very close.

The situation for A_3B type alloys is somewhat different from that of AB type alloys. The Brillouin zone structure of A_3B type ordered alloys is a rhombic dodecahedron. In other words, this has twelve {110} faces as compared to four {110} faces for AB type alloys. The introduction of a superperiod in one direction affects eight of these twelve {110} faces. However, the manner of the separation of these two groups of four Brillouin zone faces is exactly the same as in the case of AB type alloys. Therefore, the relation between the electron atom ratio and the period M is given by the same relation as in the case of CuAu II. Actually, the period of long period superlattices observed in alloy series such as Ag-Mg, Au-Cd, Au-Mn, Au-Zn, Cu-Pd, Cu-Pt etc. can be given by the same equation with similar truncation factors.