Effect of Additional Elements on the Period of CuAu II and the Origin of the Long-Period Superlattice

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A detailed study on the effect of additional elements on the period of CuAu II was made to investigate the origin of the long-period superlattice. Single crystals of CuAu were made by the successive evaporation of Au and Cu onto a heated NaCl substrate. A known amount of the additonal element was evaporated onto the CuAu film and diffused in by appropriate annealing techniques. The effect of the addition of 16 different elements in varying concentrations on the domain size of CuAu II was determined using electron diffraction. The addition of group III elements Al, Ga, and In of up to 25 atomic percent was found to decrease the average domain size M (half-period) with increasing concentration of the element (from 5 to 1.5). Sn, Mn, and Zn incorporated into CuAu also decreased the domain size. Nickel and Pd in small amounts increased the domain size, as did Ag and concentrations of Cu and Au above the stoichiometric proportion. From the analysis of all the data, a definite relation was found to exist between the electron-atom ratio and the domain size. From the experimental data, a model based upon the stabilization of alloy phases using the Brillouin zone theory was formulated to show

the variation of the electron-atom ratio e/a with the domain size M. This relation is given by the following formula: $e/a = (\pi/12t^3)(2\pm 1/M + 1/4M^2)^{\frac{1}{3}}$. Here t is a truncation factor which in most cases has a value of around 0.95. The agreement between theory and experiment is very good. In addition, the model was applied to other alloy systems where long-period superlattices are formed and was found to give a good explanation for the stabilization of these structures. The theory provides two regions depending upon the electron-atom ratio where all the predictions are reversed. The Cu-Au system and the Cu-Pd system are examples of these two regions, respectively. The theory not only predicts the variation of the domain size with the electron-atom ratio, but also predicts the concentration dependence (without changing the electron-atom ratio) and the temperature dependence, the distortion of the lattice, the appearance of one- and two-dimenional antiphase domains and other characteristics of long-period superlattices which are in accord with the experimental data on many alloy series.

I. INTRODUCTION

AMONG the numerous types of superlattices found in alloy systems, there is a group that is classified as "long-period superlattices."[1] These are superlattices with stable antiphase domains of a definite size, and hence they form periodic structures. The superlattice CuAu II in the Cu-Au alloy system is a classic example of this type of structure.

Copper and gold form a continuous solid solution at all compositions and form several superlattices, Cu_3Au, CuAu, $CuAu_3$, all of which have been extensively investigated.[2] CuAu II is a modification of the superlattice formed near the stoichiometric composition CuAu. The alloy at this composition is in the disordered state above 410°C and has a face-centered cubic structure. Below 380°C the alloy becomes ordered and each two of the four simple cubic sublattices of the fcc structure now contain all Cu and all Au atoms, respectively. This structure, known as CuAu I, is shown in Fig. 1(a). Alternate (002) planes contain either all Cu or all Au atoms and thereby cause a contraction in the c direction. This results in a tetragonal face centered structure with a c/a ratio of 0.92. The superlattice CuAu II is a modification of the CuAu I structure and is stable in the temperature range between the CuAu I and disordered phases, i.e., from about 380°C to 410°C. The unit cell of this structure is orthorhombic and is shown in Fig. 1(b). It is seen that the CuAu II structure is composed of unit cells of the CuAu I

type and is characterized by the existence of antiphase, or "out of step" boundaries at each five unit-cell lengths in the b direction. The "out of step" which occurs at this boundary is equivalent to a lattice shift of $\frac{1}{2}(\mathbf{a}+\mathbf{c})$ and the distance between each antiphase boundary is specified by a distance Mb and is described in terms of a "domain size" M. For CuAu II at the stoichiometric composition, $M=5$. This type of structure is called a one-dimensional long-period superlattice with a period $M=5$. As a result of the change in symmetry in the atomic arrangement the original unit cell itself also deforms in the b direction, thereby causing $b/a>1$ in addition to the deformation in the c direction.

The superlattice CuAu II has been investigated by many researchers since its discovery by Johansson and Linde using x-ray methods.[3] Not only the structure

O – Cu ATOM
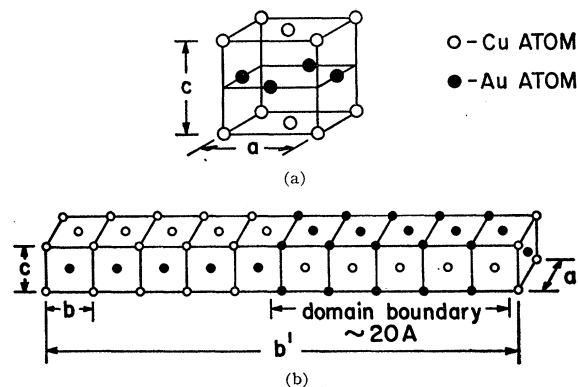$\bullet$ – Au ATOM

(a)

(b)

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

[1] See for example L. Guttman, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 174.

[2] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 198.

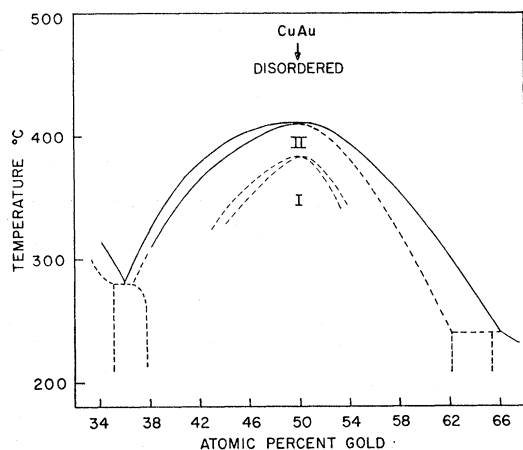[3] C. H. Johannson and J. O. Linde, Ann. Phys. 25, 1 (1936).

and physical properties in the equilibrium state, but also the kinetics of the formation of this superlattice have been investigated.[4] These data show that the long-period superlattice CuAu II is really an equilibrium phase and not a transition stage between equilibrium phases. Since the usual order-disorder transformation is a nucleation and growth process, and a fcc lattice has four equivalent sublattices, the ordered phase (CuAu I type) can nucleate at four different sublattices and grow. These nuclei meet together and form an antiphase structure just as a crystal forms a polycrystalline structure. If this were the origin of the antiphase, however, the size of the antiphase regions would be different depending upon the history of the treatment, and would eventually form a single domain structure by prolonged annealing. However, CuAu II has a definite antiphase domain size $M = 5$, irrespective of the thermal history. Also, recent electron microscopy and diffraction work utilizing the thin film technique[5,6] has indicated that CuAu II nucleates and grows from both the disordered state and from the ordered CuAu I state. These results, in addition to specific heat data[7] which show that latent heats are observed at both the transition temperatures, unequivocally show that CuAu II is really an equilibrium state.

Many other long-period superlattices have been found in alloys, and in addition to the one-dimensional long-period superlattices of the CuAu II type, there exist two-dimensional long-period superlattices. The frequent occurrence of these superlattices clearly shows that they are common structures which can be more stable than the usual superlattices. Since such long-period super-lattices are equilibrium phases, the origin of the stabili-

zation as well as the period M, etc. should be explained by an equilibrium theory. However, it is also clear that this kind of structure cannot be explained by a pair interaction model usually adopted in explaining the order-disorder phenomenon, because for this purpose, extremely long distance interaction is involved. Consequently, the type of theory required must be related to the collective behavior of the crystal in some form or other. That is, it should be related to some sort of behavior of the free electrons, or to some sort of collective behavior of the atoms, such as atomic vibration, etc. The first aim of the present research is therefore directed to experimentally determine what factor contributes most to the stability of long-period structures.

In order to obtain information concerning the origin of the stability of long-period superlattices, from the above reasoning, either the number of free electrons of the system or the mass or the size of the constituent atoms should be changed systematically, and the change in properties, especially the period and the stable temperature range, should be observed. Although some research has been done in this direction,[8–10] the data are limited and therefore a systematic supplement to the existing data is necessary. In other words, many different elements in various quantities must be added to CuAu II and their effect on the domain size M should be observed. For this purpose, single crystals of CuAu are
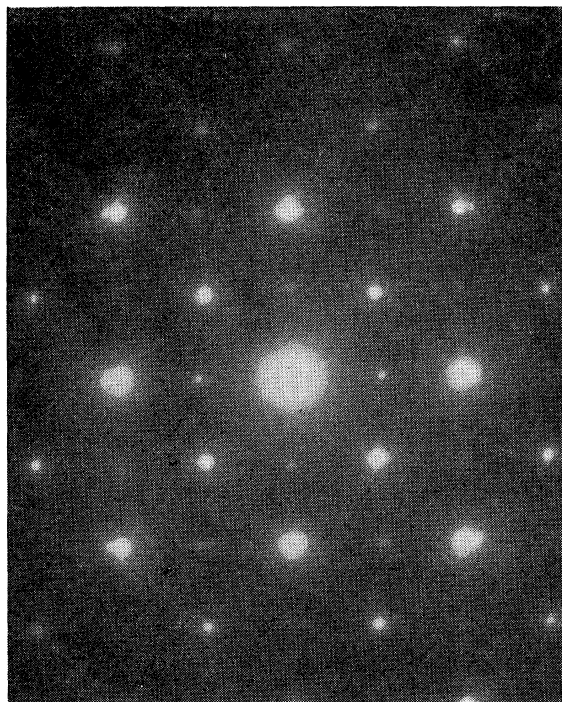

FIG. 3. Electron diffraction pattern of CuAu I.

[4] For example, G. Borelius, J. Inst. Metals 74, 17 (1947); G. J. Dienes, J. Appl. Phys. 22, 1020 (1951).
[5] S. Ogawa and D. Watanabe, J. Phys. Soc. Japan 9, 475 (1954).
[6] D. W. Pashley and A. E. B. Presland, J. Inst. Metals 87, 419 (1958).
[7] M. Hirabayashi, S. Nagasaki and H. Maniwa, Nippon Kinzoku Gakkaishi B14, 1 (1950).

[8] S. Ogawa, D. Watanabe, H. Watanabe, and T. Komoda, J. Phys. Soc. Japan 14, 936 (1959).
[9] K. Schubert, B. Kiefer, M. Wilkens, and R. Haufler, Z. Metallk 46, 692 (1955).
[10] E. Raub and P. Walter, Z. Metallk 41, 240 (1950).

far superior to polycrystalline material, and in addition, the alloy should be annealed long enough to allow a high degree of order and homogeneity in each case. Unfortunately both the single-crystal fabrication and the annealing process are quite time consuming for bulk material, and therefore it is quite impractical to do this type of research with bulk crystals. In order to avoid this difficulty, we adopted a thin-film technique.

In the work to be described below, we show how the thin-film technique was employed to obtain systematic data necessary to pinpoint the origin of the long-period superlattice. These data were then employed in formulating a theory to explain the origin of the long-period superlattice.

II. EXPERIMENTAL METHOD

The thin film technique has been used successfully by several groups, most recently by Raether,[11] Ogawa et al.,[5] and Glossop and Pashley.[12] The method consisted of preparing single crystal thin films of CuAu by successive evaporation of Au and Cu onto a single crystal NaCl substrate held at an appropriate temperature. Various amounts of a third element were then evaporated onto the film, which was then homogenized by appropriate annealing procedures. The films were then examined by electron diffraction. The methods are described in detail below.
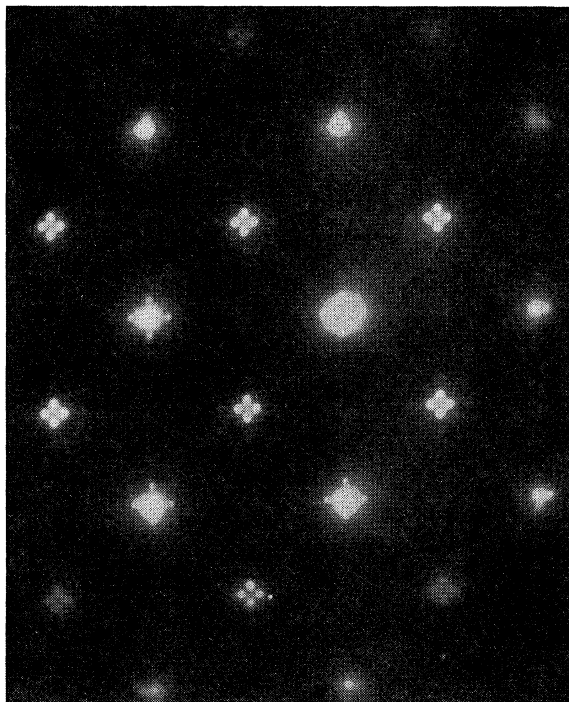

FIG. 4. Electron diffraction pattern of stoichiometric CuAu II.

[11] H. Raether, Z. angew. Phys. 4, 535 (1952)
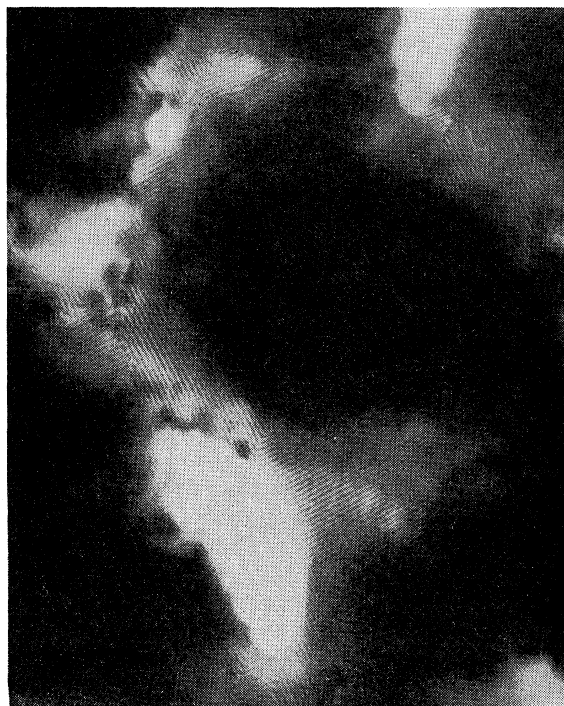[12] A. B. Glossop and D. W. Pashley, Proc. Roy. Soc. (London) A250, 132 (1959).

FIG. 5. Electron micrograph of CuAu II showing antiphase domain structure. Magnification 320 000×.

A. Preparation of Samples

Single-crystal films of CuAu about 300–400 A thick were made by first evaporating completely a measured amount of Au from a tungsten boat onto a heated, freshly cleaved NaCl substrate. For best results in this initial stage, the NaCl was first heated to 500°C and then cooled to 400°C, at which temperature the Au was evaporated. An epitaxial growth of a (001) orientation of the Au film on the (001) face of the NaCl results, even though the misfit is quite large ($\sim 28\%$).[13] Without changing the evaporation geometry, a calculated amount of Cu, required to form the 50-50 atomic percent alloy, was completely evaporated onto the Au film, which was reheated to about 350°C. The film was annealed on the NaCl at this temperature for about one hour, although homogenization is completed at this temperature in about half an hour. The vacuum used in these evaporations was 5×10^{-5} mm Hg or less, and was found to be completely satisfactory for this purpose.

The CuAu film was then removed from the substrate by immersing the NaCl in water. Samples of the film were collected on standard 200 mesh stainless steel electron microscope screens. Depending upon the initial size of the CuAu film, as many as 20–30 samples could be collected from each film.

For the addition of the third element, the samples were placed in stainless steel holders which could be

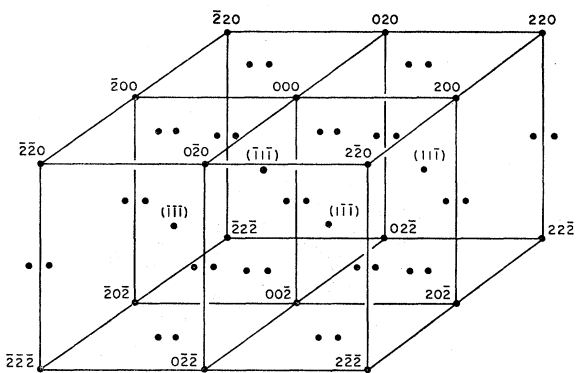[13] L. Bruck, Ann. Phys. 26, 233 (1936).

FIG. 6. Reciprocal lattice for the CuAu II structure.

attached to furnaces in the evaporation system. The identical evaporation geometry used in preparing the CuAu films was reproduced, and a measured quantity of the third element was completely evaporated. The samples were then annealed at an appropriate temperature for diffusion of the third element into the film. The annealing temperature was such that the vapor pressure of the added element was less than 10^{-6} mm Hg. Only those elements which could be evaporated from W boats and which have low vapor pressures near 350°C were used.

The composition of the resulting alloys could be checked by measuring their lattice constants and comparing with the known data on bulk material, since the lattice constants of the alloys in film form agree very well with those of bulk materials. This method was frequently used, and, in most cases, the value agreed with the calculated one. In the majority of the cases, however, we used the values obtained from the known evaporated amount. This was imperative in cases where no data on bulk material was available. Consequently, there is a slight ambiguity about the composition of the ternary alloys.

B. Determination of Phase and Domain Size

All samples were examined in a RCA-EDU electron diffraction unit having an average accelerating voltage of about 50 kv. The samples were placed in a heating stage in the EDU so that patterns could be obtained at various annealing temperatures. In this way, pertinent data was obtained on the phase changes from CuAu I to the disordered phase. The equilibrium phase diagram around CuAu is shown in Fig. 2 for reference. Annealing times required to reach equilibrium for the films in the temperature range of interest were of the order of one hour. Diffraction patterns were obtained showing the change in the film from the CuAu I phase to CuAu II and finally to the disordered phase. That the formation of CuAu II is a nucleation and growth process either from the CuAu I or from the disordered state could be confirmed by observing continuously the development of the superlattice spots characteristic

of CuAu II inside the camera. Such a nucleation and growth process has also been observed in CuAu II by electron microscopy by Pashley et al.[6] In the case of the alloys with a third element, the times necessary for the transformations to reach equilibrium were not investigated in detail and consequently an accurate transformation temperature could not be obtained. However, the data could be used to show the general trend of the transformations CuAu I ↔ CuAu II ↔ disordered for these ternary alloys.

In some cases, it was convenient to investigate the films in the EDU at room temperature. This necessitated the rapid quenching of the film from the annealing temperature to room temperature. Although the time required to reach the equilibrium state is short, both the disordered and CuAu II state can be obtained by rapidly quenching the thin film. For this purpose a small Vycor vacuum furnace was constructed for annealing the films. Helium gas was let into the system as a heat conductor and liquid N_2 was used as the coolant in the quenching process. The films could be cooled from 400°C to room temperature in 30 sec using this apparatus. However, the examination of the films at high temperatures in the EDU could be done without any difficulty, and consequently the quenching technique was seldom necessary.

The nature of each phase and the domain size M of CuAu II were obtained by careful examination of the diffraction patterns. In the disordered state, the alloy shows spots which are characteristic of a fcc lattice. Since the plane of the film normal to the electron beam is the (001), the main spots observed are (200), (220), etc. When the superlattice CuAu I is formed, superlattice spots at the {110} positions are observed. An electron diffraction pattern of CuAu I is shown in Fig. 3. In the photograph, faint {100} spots are also observed. These are due to the presence of domains with the c axis in the plane of the film, but in most cases the c axis
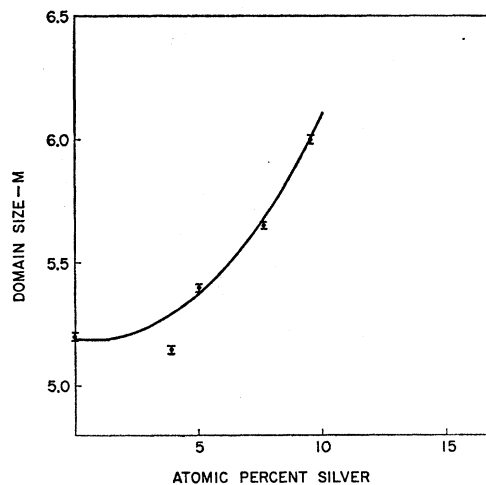

FIG. 7. Domain size M vs concentration of Ag in CuAu II.

is perpendicular to the plane of the film. When the CuAu II phase is formed, the superlattice spots separate into two, due to the added periodicity in the b direction. A typical CuAu II pattern is shown in Fig. 4. The appearance of four intense superlattice spots instead of simply two is due to the nucleation of antiphase domains in orthogonal directions, there being two equivalent b directions with a common c axis, in the (001) film. The nucleation of the antiphase domains in the film can be seen in the electron microscope. Such a pattern, taken with a Hitachi HU-11 electron microscope, is shown in Fig. 5. Alternate dark lines in the picture represent the antiphase domain boundaries, and show the growth of the domains in orthogonal directions. A detailed explanation of the CuAu II diffraction pattern has been given by Ogawa and Watanabe,[5] and by Glossop and Pashley.[12] The reciprocal lattice of the CuAu II structure is shown in Fig. 6.

In determining the domain size M, we need only to consider 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. Thus the domain size M could be determined to a fair degree of accuracy from measurements on the single crystal diffraction patterns when the spots are sharp. The sharpness of the spots is indicative of the regularity of the antiphase domain size.

III. EXPERIMENTAL RESULTS

A total of sixteen different elements of high purity covering most groups in the periodic system were added to the CuAu films and their effects noted. At least five different concentrations of each element tested were added to the film. These results are discussed in detail below.

A. Copper, Silver, and Gold

The addition of either Cu or Au above the stoichiometric composition resulted in an increase in the domain size M. The data obtained was very similar to that reported by Ogawa and Watanabe.[5] The domain size increased toward the value 6 as the Au or Cu content
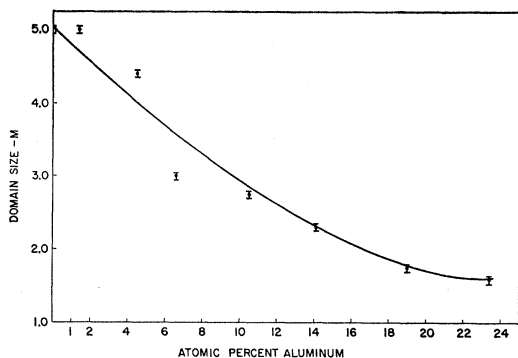

FIG. 8. Domain size M vs concentration of Al in CuAu II.
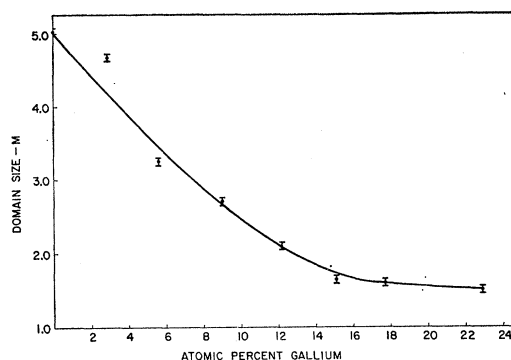

FIG. 9. Domain size M vs concentration of Ga in CuAu II.

increased to 60 atomic percent. At 55% Cu, the domain size was 5.75; but at 60% Cu only a mixed phase of CuAu I and CuAu II was obtained. At 55% Au, the domain size was 5.5. The addition of Ag into CuAu also resulted in an increase in domain size. The change in domain size with Ag content is shown in Fig. 7. The CuAu I–CuAu II transition temperature T_{c1} was found to be lowered slowly with added Ag content. For example, at 7.5% Ag, the CuAu II phase still occurred at 330°C.

B. Aluminum, Gallium, and Indium

The addition of either Al, Ga, or In caused a systematic decrease in domain size with concentration of the added element. This is shown in Figs. 8–10. It is interesting to note that the change in domain size with concentration of solute for Al and Ga is practically identical. In both cases, the CuAu could accommodate up to 23% of the solute and still maintain the same structure. An electron diffraction pattern of CuAu II with added Al is shown in Fig. 11. The large increase in the separation of the superlattice spots is apparent and is indicative of the decrease in domain size.

For the CuAu-Al samples, the stable region of CuAu II was found to be lowered with added concentration of Al with T_{c1} being about 370°C for Al content of 5% and greater. The lowering of the stable region was more evident in the CuAu-Ga system. For a sample containing 12% Ga, the structure was still the disordered one after annealing for 5 hours at temperatures down to 275°C. The transition temperature for the disordered-CuAu II phase change, T_{c2}, was near 300°C for CuAu containing 6% Ga.

The domain size decreased rapidly with the addition of In, reaching a value of near 2 at In concentrations of only 15%. The transition temperature T_{c2} was found to decrease to temperatures of 300°C and lower for large concentration of In.

C. Germanium and Tin

For CuAu films containing 3.6% to 17.3% Ge, there was no occurrence of the CuAu II phase. In going from
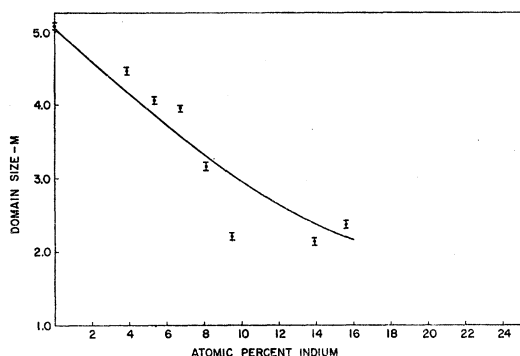
FIG. 10. Domain size M vs concentration of In in CuAu II.

CuAu I to the disordered phase, the CuAu II phase was not detected. In addition, the Ge did not completely diffuse into the film since Ge rings were superimposed on the CuAu pattern even after prolonged annealing. At 17.3% Ge, the film became polycrystalline with preferred orientation.

For concentrations of Sn less than 8%, a decrease in the domain size was observed. This is shown in Fig. 12. Above 8% Sn, no CuAu II superlattice was detected. In the region where CuAu II occurred, T_{c2} was in the neighborhood of 300°C.

D. Antimony and Bismuth

The addition of Sb or Bi in small amounts appeared to have no effect on the domain size in CuAu II. Moreover, neither element appeared to diffuse completely into the film, as indicated by a superposition of spots on these diffraction patterns. For Bi concentrations greater than 4.5%, the film became polycrystalline. For concentrations of Sb greater than 7%, no CuAu II was detected.

E. Beryllium and Magnesium

No effect on the domain size of CuAu II was noticed with the addition of up to 37% Be. The Be did not diffuse into the film as evidenced by a smear of spots superimposed on the CuAu II pattern.

There was no change in the domain size of the CuAu II for samples containing up to 20% Mg. Some faint broad rings were noticeable in the pattern, but indications were that the Mg had diffused into the film. For films containing 20%–30% Mg, a new complex single crystal diffraction pattern was observed, which was not analyzed.

F. Chromium, Manganese and Iron

The incorporation of up to 25% Cr into CuAu did not affect the domain size of the CuAu II formed. Some polycrystalline rings due to Cr were superimposed on the pattern and indicated that not all the Cr had diffused into the film. The CuAu II phase occurred in the

same temperature region as for the stoichiometric compound.

The addition of Mn to CuAu caused a decrease in the domain size, similar to that found for CuAu-In. The decrease in M with concentration of solute is shown in Fig. 13. Again, the transition temperature decreased as the solute concentration increased, so that at 9% Mn, T_{c2} was about 350°C.

The addition of Fe into CuAu appeared to have little effect on the domain size. The diffraction pattern showed that the Fe had diffused in but no apparent change was noticed for M or for the transition temperatures.

G. Nickel and Palladium

The CuAu II phase did not form in films having concentrations of Ni greater than 5%. For smaller concentrations, the domain size increased, and at 2% Ni had a value of 5.25 while at 5% Ni had a value of 6.0. The transition temperature T_{c2} was practically unchanged in the range where CuAu II was still formed. However, in the range where CuAu I was the only ordered phase, the transition temperature increased so that CuAu I existed in the range where ordinarily CuAu II would be stable.

Films containing Pd acted in a similar fashion. Here, the CuAu II phase was found only at Pd concentrations less than 1%. At 0.5% Pd, $M=5.5$ while at 0.8% Pd, $M=5.8$. For larger concentrations of Pd, CuAu I was the only ordered phase detected. Here the CuAu I phase was found to be stable at much higher tempera-
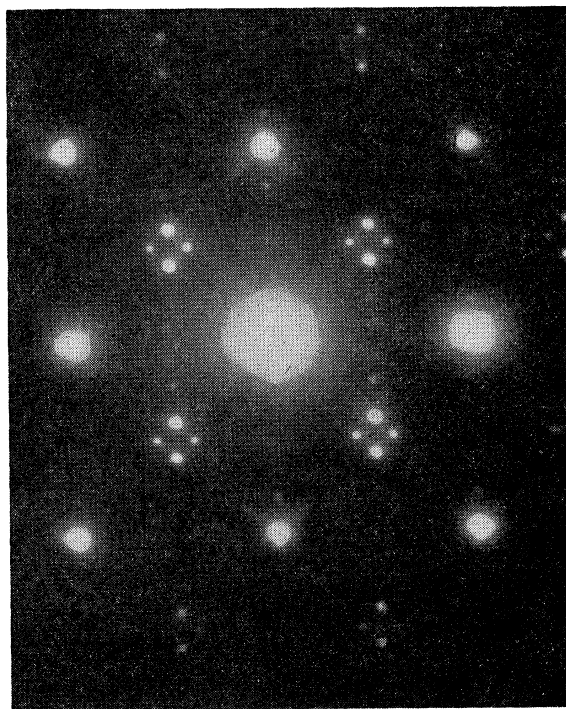

FIG. 11. Electron diffraction pattern of CuAu II containing 5.8% Al showing increased separation of superlattice spots.

TABLE I. Summary of experimental results, showing effect of additional elements on the domain size M, and listing the size factor for each element.

Element	Gold-schmidt radii(A)	$d/2$(A)	Size factor (Au)	Size factor (Cu)	Effect on domain
Au	1.44	1.44	0	+12.5	Increase
Cu	1.28	1.28	−11.1	0	Increase
Al	1.43	1.43	−0.695	+11.7	Decrease
Ga	1.39	1.22	−3.47	+8.60	Decrease
In	1.57	1.62	+9.02	+22.6	Decrease
Ge	1.39	1.22	−3.47	+8.60	Increase
Be	1.13	1.11	−21.5	−11.7	None
Pd	1.37	1.37	−4.85	+7.03	Increase
Bi	1.82	1.55	+26.4	+42.2	None
Sn	1.58		+9.72	+23.4	Decrease
Mg	1.60	1.60	+11.1	+25.0	None
Cr	1.28		−11.1	0	None
Mn	1.31		−9.02	+2.34	Decrease
Sb	1.61	1.45	+11.8	+2.58	None
Ag	1.44	1.44	0	+12.5	Increase
Fe	1.27	1.24	−11.8	−0.775	None
Ni	1.24	1.24	−13.9	−3.3	Increase
Zn	1.37	1.33	−4.85	+7.03	Decrease

tures than for the stoichiometric alloy. The change in the transition temperature from CuAu I to the disordered phase with Pd content is shown in Fig. 14. It is seen that this transition temperature is about 100° higher than the usual T_{c2} for stoichiometric CuAu II.

H. Zinc and Cadmium

An attempt was made to incorporate Zn and Cd into the CuAu films. Both these elements have high vapor pressures at temperatures where one would expect the CuAu II phase to occur. Consequently, it was difficult to incorporate these elements into the films with any degree of reproducibility. Attempts to diffuse Cd into CuAu were unsuccessful. However, by careful evaporating and annealing procedures, Zn was incorporated into CuAu. As reported by Ogawa et al.,[8] it was found that Zn in CuAu decreased the domain size in a manner similar to CuAu-Al. However, quantitative data could not be obtained because of the ambiguity of the composition.

A summary of the effect on the domain size for the elements tested is given in Table I, together with the atomic size factors.
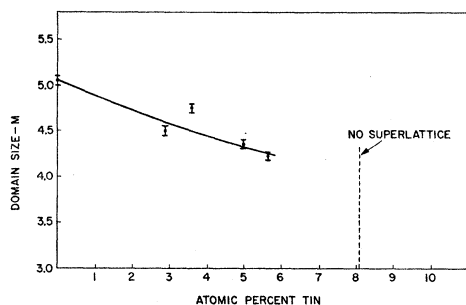

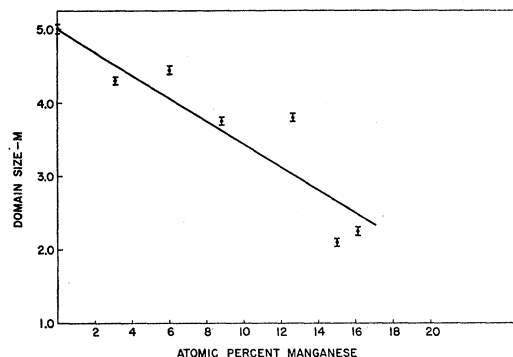FIG. 12. Domain size M vs concentration of Sn in CuAu II.

FIG. 13. Domain size M vs concentration of Mn in CuAu II.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

Among the sixteen elements added, several were found not to be soluble in CuAu in any appreciable amount. These cases were easily identified by observing the diffraction patterns, which showed superposed rings, diffuse hollows, destruction of the single-crystal spots, change in patterns, etc. In such cases, of course, we could not observe any change in the period of CuAu II. These elements were Sb, Bi, Be, Cr, and possibly Mg may also be included in this group. In the case of Mg, a concentration of greater than 20% Mg seemed to change the CuAu phase to a new single cyrstal ordered phase, which we did not analyze. The lack of solubility of these elements may be explained in terms of the size factors which, in most cases, are unfavorable as can be seen in Table I.

In the case of Fe, it appeared that the Fe diffused into the CuAu alloy, since no defects in the diffraction pattern were noticed. At the same time, we did not observe any noticeable change in the domain structure of CuAu II. This fact casts serious doubt on the assumption that the Fe actually diffused into the film. In the case of bulk, Fe is not very soluble in either Cu or Au, and although we could not find any extensive study on the Cu-Au-Fe system, it is not very likely that Fe is soluble in large amounts in the alloy. Of course there is no guarantee of this fact in the case of thin films since the properties of the film may be different from that of bulk. Although the lattice constant of the alloy was changed somewhat by the addition of Fe, it was not possible to determine the iron content since the lattice constant data on this system are not available. As a result, we did not include the data on Fe in the final analysis.

In the other cases, an extensive solubility was found in the temperature range of the CuAu II phase. In some cases, the solubility seemed to be larger in films than in bulk material. It is quite possible that the increased solubility in the thin films may be due to the increased number of vacancies and other defects which occur in larger number than for bulk material. These defects would increase the diffusion rate of foreign atoms at relatively low temperatures, as indicated, for example,
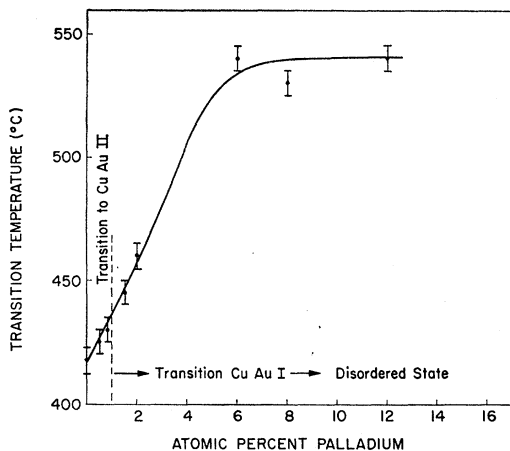
FIG. 14. Change in transition temperature from ordered to disordered state for CuAu II with concentration of Pd.

by the diffusion of Cu into the single-crystal Au described previously. Nevertheless, the lattice constants of the alloys in thin film form agree with those of bulk material within 0.1%. Because of the wide solubility range, the dependence of the domain size M on the amount of the alloying element could be obtained with a fair degree of accuracy.

There is some question concerning the interpretation of the domain size thus determined, since M changes continuously with the alloying element and therefore does not usually take an integral or half integral number as would be anticipated if the domains were of a regular size as shown in Fig. 1(b). The nonintegral value of M can be interpreted as a mixture of different domain sizes. From the diffraction pattern alone, however, one cannot tell the true situation about the nature of the mixture. As long as the spots are as sharp as the original CuAu II pattern, however, it is legitimate to speak of the average size of the domains. Therefore, we will, for the moment, interpret the value of M as the size of the domains without going into the nature of the mixture in detail.

Even in the original CuAu II, there is still a controversy concerning this point since one obtains values of M greater than 5 for alloys which do not have the stoichiometric compositions, as shown in the data. It has been shown that sharply separated points with a nonintegral value of M should be observed if two domain sizes M' and M'' mix either regularly or quite randomly.[14] Therefore, the sharpness of the separated spots does not necessarily mean that the domain size is a definite nonintegral value. As previously mentioned, however, it is possible to resolve the antiphase domain in the electron microscope and to make a direct observation of the domain length. This has been done by Ogawa et al.[15] and by Pashley and Presland[16] on slightly nonstoichio-

metric CuAu II. According to Ogawa et al., measurements of the length of the domains show double maxima at 5 and 6, indicating that a mixture of these two domain sizes exist in the alloy. On the other hand, Pashley and Presland found only a single maximum at 5.5 and they interpreted this as corresponding to a CuAu II structure containing 11 cells of the CuAu I type. Because of this confused situation, there is at present, no definite way of deciding the true nature of nonintegral M values. An investigation of CuAu II films containing Al and having small M values is being carried out using an electron microscope in order to clarify this point.

Although there are many possible causes for the origin of the periodic structure, these should be related in some way or other to the collective behavior of the crystal. Then the factors which should be taken into account are the number of free electrons per alloy atom, the weight of the atoms, the size of the atoms, etc. With this assumption, we first plotted the domain size M against the number of free electrons per atom (electron-atom ratio, e/a) of the system, taking into account the valency of the additional elements. This curve is shown in Fig. 15, and one can see a regularity between e/a and M. The electron-atom ratio e/a, was calculated according to the composition of the alloy. Here, the number of electrons was taken to be zero for Ni and Pd, one for Cu, Ag and Au, two for Mn and Sn, and three for Al, Ga, and In. The valency of two assigned to Mn and Sn may be a cause for argument. However, if one thinks of a valency for Mn in terms of a compound such as MnO and the fact that an excellent agreement was obtained in the e/a vs M curve using this value, it seems that Mn behaves as a divalent atom in the alloy. A similar argument can be applied to the case of Sn. The scatter of the points in the figure may be due to the uncertainty in the compositions of the alloy films, as previously pointed out.

Because of this regularity, the data was replotted to find an exact relation between e/a and M. Figure 16 shows a plot of e/a vs $1/M$, and it can be seen that there exists a linearity between these two quantities. It is important to note that the linear curve cuts the ordi-
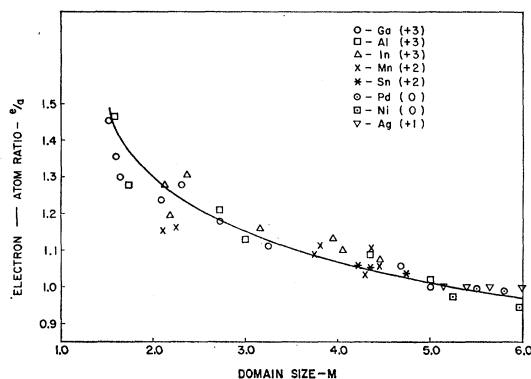
[14] K. Fujiwara, J. Phys. Soc. Japan 12, 7 (1957).
[15] S. Ogawa, D. Watanabe, H. Watanabe, and T. Komoda, Acta Cryst. 11, 872 (1958).
[16] D. W. Pashley and A. E. B. Presland, Structure and Properties of Thin Films (John Wiley & Sons, Inc., New York, 1959), p. 199.

FIG. 15. Electron-atom ratio vs domain size M using the indicated valences for the elements tested.

nate at $e/a=0.85$, indicating that M becomes infinite at $e/a=0.85$. Here $M=\infty$ means the prefect CuAu I type superlattice, while $M=0$ means the disordered state. The above relation indicates that the period becomes longer as e/a becomes smaller until finally CuAu II vanishes at $e/a=0.85$ and only CuAu I is formed. Schubert,[9] in assembling data on several one- and two-dimensional long-period superlattices, has found a similar relation between e/a and M. The meaning of his data is slightly different from ours, since we have considered only the case of CuAu II. The curve should be different for each alloy series.

There is a slight dependence of M on the concentration of Cu or Au. That is, increasing Cu or Au from the stoichiometric composition results in an increase in M. It may be said that there is a slight difference in the effective number of free electrons between Cu and Au. However, the fact that the M value increases with the addition of either Au or Cu means that this possible difference in the number of electrons is not the important factor. Similarly, the difference in size or weight of the Au and Cu atoms would not be responsible for the change in M for the same reason.

The temperature change causes a similar effect. By lowering the temperature in the CuAu II stability range a slight increase in M is found,[5] although we could not substantiate this fact with confidence since the range of CuAu II is so narrow. It is also apparent in this case, that the number of free electrons, size and weight of atoms would not be responsible for this change. These effects will be discussed more fully later.

The data clearly show that there is an intimate relation between the stability range of CuAu II and the M value. For example, the transition temperature T_{c1} is raised by the addition of such elements as Pd or Ni which increase the period, while there is a trend to decrease T_{c1} as M decreases. In the present investigation, however, quantitative data concerning this relation were not taken.

Other than the definite relation between the value of M and the number of electrons per atom of a system, no systematic dependence of M on the size factor or weight of atoms of the additional element could be found. From the experimental results, it is now clear that the origin of the long-period superlattice is intimately connected to the electron-atom ratio of the system. The change of the concentration and the temperature as well as the change of the degree of order, seem to have a secondary effect on the period. Thus, the first aim of this research was successfully attained since the experiments showed conclusively that the electron-atom ratio is the deciding factor for determining the period of the superlattice of CuAu II.

V. THEORETICAL INTERPRETATION OF THE ORIGIN OF THE LONG-PERIOD SUPERLATTICE

The general theoretical treatment of the stabilization of long-period superlattices should be as follows. First
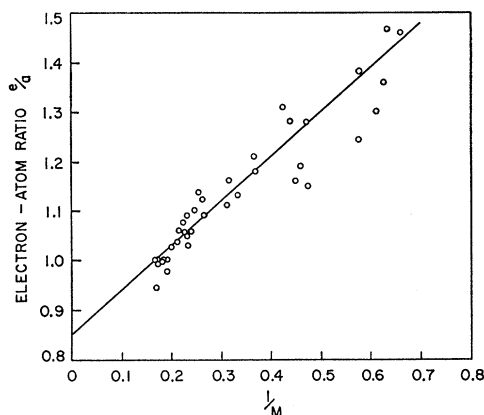

FIG. 16. Electron-atom ratio vs the reciprocal of the domain size M for additional elements in CuAu II.

it should be an equilibrium theory and therefore should explain the existence of the long-period structure as an equilibrium phase. It should not be a theory which, although it can predict the existence of the antiphase structure at some intermediate stage, eventually leads to the equilibrium state given by the CuAu I type structure. The difference of the configurational part of the entropy between CuAu I and CuAu II should be almost negligible. Therefore, the origin would be either a special form of entropy term which is directly connected to the periodic antiphase domains or entirely an internal energy term. Although CuAu II exists only in the intermediate temperature range, most of the long-period superlattices found in other alloy systems are true equilibrium phases at low temperatures. Therefore, the origin would most probably be connected with the stabilization due to the internal energy term and not the entropy term.[17]

Second, it is apparent that a usual pair-type model with a nearest neighbor interaction cannot explain this structure. The numbers of pairs of each kind of atoms are not very different between CuAu I and CuAu II, and the introduction of "out of step" boundaries increases instead of decreases the energy. Thus it is necessary to introduce a kind of long-range interaction due to the collective behavior of the crystal which will lead to a lowering of the energy of the system by the introduction of extra periods in the atomic arrangement, in addition to a short-range interaction which leads to the ordered state. The latter, however, increases the energy of the system by introducing the extra period. Thus, the equilibrium size of the period would be determined by the sum of these energy terms. The situation is quite similar to that encountered in the problem of the screw-type arrangement of spins in magnetism.[18] In this sense, it also appears possible to explain such a phenomenon to

[17] For detailed thermodynamical arguments concerning the two phases, refer, for example, to B. A. Roberts, Acta Met. 2, 597 (1954); R. A. Oriani, Acta Met. 2, 608 (1954); R. A. Oriani and W. K. Murphy, J. Phys. Chem. Solids 6, 277 (1958).

[18] A. Yoshimori, J. Phys. Soc. Japan 14, 807 (1959); J. Villain, J. Phys. Chem. Solids 11, 303 (1959).
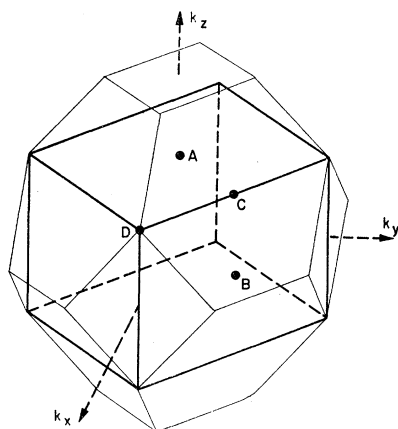
FIG. 17. Brillouin zone structure for CuAu: Thin lines represent zone for disordered phase; thick lines represent zone for ordered CuAu I phase.

some extent with a pair interaction model by introducing competing interactions of different interaction ranges.[19]

However, it is now clear from the experimental results that the period has a definite dependence on the electron-atom ratio. Thus it is apparent that the free electrons of the system are responsible for the stabilization of the periodic structure and therefore we can rule out the possibility that the collective behavior of the constituent atoms, the atomic vibrations for example, is the origin of the antiphase structure. At the same time, we can rule out the competing interaction model mentioned in the previous paragraph, because it is hardly conceivable that two types of such interactions are dependent only on the electron-atom ratio, and not on the kind or size of the atoms, etc.

Among the several possible mechanisms which depend only upon the number of free electrons, the most conceivable mechanism would be the stabilization of the kinetic energy of the free electrons due to the splitting of the Brillouin zone by the introduction of an extra period. This idea was first adopted by Jones[20] in the explanation of phase boundaries in alloy systems and has since been successfully applied to many problems of alloys. Other possibilities could include the stabilization of special sinusiodal variations of some properties of the free electrons, such as the spin density fluctuation or the mass density fluctuation. The Brillouin zone mechanism for CuAu II has been suggested very vaguely by Nicholas,[21] Slater,[22] one of the authors,[23] and possibly others. However, no detailed discussion has been given thus far. On the other hand, an explanation based on a type of mass density fluctuation of free electrons

has been given for the long-period superlattice by Schubert.[24] Although all mechanisms should cause a splitting of the Brillouin zone as a result of having an extra period, the essential question is whether or not the splitting of the Brillouin zone itself is responsible for the stabilization.

These possibilities were examined in detail in conjunction with the experimental data, and it was concluded that the splitting of the Brillouin zone itself is the principal origin for the stabilization of the long-period structure. This is discussed in detail below.

A. Brillouin Zone Structure of CuAu

The first Brillouin zone of the disordered face-centered cubic alloy is the well known truncated octahedron. The zone is bounded by the planes $\{111\}$ and $\{200\}$ as shown by the thin lines in Fig. 17. The volume of the zone is equal to $4/a^3$ (a=lattice parameter) and corresponds to two electrons per atom. The volume of the inscribed sphere is 0.681 of this zone, and can include 1.362 electrons per atom. Since we can ascribe one electron per atom to both Cu and Au, the Fermi surface is well inside of the Brillouin zone and would be nearly spherical.[25] When the alloy forms the CuAu I ordered structure, the Brillouin zone splits because of the new periodicity, and a new Brillouin zone is formed, bounded by $\{001\}$ and $\{110\}$ planes as shown by the thick lines in Fig. 17. The volume of this new zone is $2/a^2c$ and can just accommodate one electron per atom.[26] Since the atomic arrangement in the unit cell of CuAu I has a tetragonal symmetry, the resulting Brillouin zone is highly anisotropic and as a result the inscribed sphere includes only 0.26 electron per atom. Free electron energies at the points A, B, C, and D on the zone boundaries in Fig. 17 are 2.4 ev, 4.8 ev, 7.1 ev, and 9.5 ev, respectively, while the energy at the surface of the Fermi sphere containing one electron per atom is 6.5 ev. Therefore, the electrons should overlap into the second zone at least in the c direction, although the overlap is a sensitive function of the energy gaps across the zone boundaries.

The introduction of the extra periodicity in the b direction due to the formation of CuAu II causes a separation of the superlattice spots in the b direction as described before, and the representation of this fact in the reciprocal lattice is shown in Fig. 6. This causes a further splitting of the Brillouin zone as shown in Fig. 18. The section of the zone cut by an (001) plane through the origin is shown in this figure. There is also a change in the $\{001\}$ zone surface, which is easily found using

[19] K. Adachi is carrying out the calculation based on this kind of model and is claiming to have obtained a fair amount of success (private communication).

[20] H. Jones, Proc. Roy. Soc. A144, 225 (1934); A147, 396 (1934); Proc. Phys. Soc. 49, 250 (1937).

[21] J. F. Nicholas, Proc. Phys. Soc. (London) A66, 201 (1953).

[22] J. C. Slater, Phys. Rev. 84, 179 (1951).

[23] H. Sato, Sci. Repts. Research Inst. Tohoku Univ. 4, 160 (1952).

[24] K. Schubert, Z. Metallk. 46, 43 (1955); Z. Naturforsch. 14a 650 (1959).

[25] According to the recent studies of the de Haas-Van Alphen effect and the anomalous skin effect, etc. there seems to be enough reason to believe that the Fermi surface of the precious metals (Cu, Au, Ag) is appreciably different from spherical.

[26] c is the lattice constant of the unit cell in the c direction. We will neglect the difference between c and a since c/a is not much different from unity.

the reciprocal lattice of the CuAu II structure. However, the overlapping of the electrons in this direction is so large, that this change in the zone surface would not affect the behavior of the electrons and consequently can be neglected. We will return to this point later. The separation of the zones shown in Fig. 18 depends upon the separation of the superlattice spots. As the period M becomes smaller, the superlattice spots separate more, and consequently the separation of the Brillouin zones increases.

The degree of overlapping as well as the degree of stabilization at the zone boundary depends very sensitively on the energy gap across the zone boundary. In this sense, a rather detailed calculation will be given to show what is involved. The energy gap across the zone boundary depends on the scattering of the free electrons by the periodic potential.[27] That is, the energy gap, ΔE_n, across a zone boundary specified by the indices $\mathbf{n}(n_1,n_2,n_3)$ is given by

$$\Delta E_n = 2|V_n|, \tag{1}$$

where the zone boundary is given by the equation

$$(\mathbf{n}\cdot\mathbf{k})+\tfrac{1}{2}n^2=0 \tag{2}$$

in $\mathbf{k}$ space, and V_n is a coefficient of the Fourier expansion of the periodic potential $V(\mathbf{r})$, given by

$$V(\mathbf{r})=\sum_\mathbf{n} V_n e^{2\pi i(\mathbf{n}\cdot\mathbf{r})/a}. \tag{3}$$

If the structure contains s atoms per unit cell, the Fourier coefficient V_n can then be expressed in the form

$$V_n=\sum_{\tau=1}^{s} A_{n\tau}e^{2\pi i(\mathbf{n}\cdot\mathbf{u}_\tau)} \tag{4}$$

where the $A_{n\tau}$'s are the coefficients of the potential for a simple cubic lattice composed of atoms of type τ, and $(\mathbf{a}_i\cdot\mathbf{u}_\tau)$ $(i=1, 2, 3)$ is the location of the atom τ from the origin of the unit cell with respect to the axes a_1, a_2, and a_3. It is clear from this expression that in the case of binary alloys, the potential V_n and hence the energy gap is given by the average of the scattering power of the A and B type atoms for the boundary corresponding to the normal one and by the difference of the scattering power of the A and B type atoms for the boundary newly formed by the formation of the superlattice. This calculation takes the same form as that of x-ray scattering, for example, from a crystal lattice.

The calculation of the energy gap for alloys based upon this development using x-ray atomic scattering factors has been carried out in detail by Jones,[20] Muto,[28] and others. For the case of a disordered binary alloy having a face-centered cubic structure, the energy gap ΔE_n is given by

$$\Delta E_n = (2e^2/a\pi n^2)|[C(Z_A-F_A)+(1-C)(Z_B-F_B)]$$
$$\times(1+e^{i\pi(n_1+n_2)}+e^{i\pi(n_2+n_3)}+e^{i\pi(n_3+n_1)})| \tag{5}$$
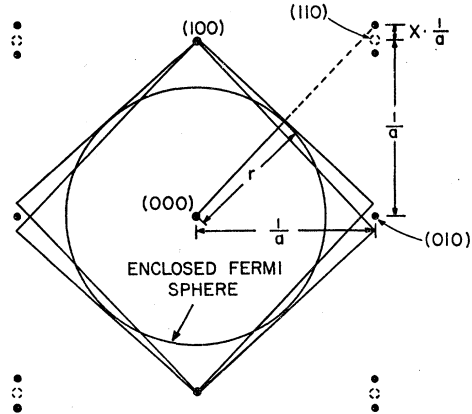

FIG. 18. Reciprocal lattice of CuAu II in a plane through the origin and parallel to the (001) plane, showing the structure of the Brillouin zone of CuAu II and of the enclosed Fermi sphere.

and for a partially or fully ordered state of the CuAu I type is

$$\Delta E_n = (2e^2/a\pi n^2)|\{C(1+S)(Z_A-F_A)$$
$$+[1-C(1+S)](Z_B-F_B)\}(1+e^{i\pi(n_1+n_2)})$$
$$+\{C(1-S)(Z_A-F_A)+[1-C(1-S)]$$
$$\times(Z_B-F_B)\}(e^{i\pi(n_2+n_3)}+e^{i\pi(n_3+n_1)})|. \tag{6}$$

Here C is the concentration of A atoms $(C\leqq\tfrac{1}{2})$, Z_i and F_i represent the atomic number and x-ray atomic scattering factor of atom i, and S is the degree of long-range order.

The calculation of the energy gap based on Eq. (6) for the stoichiometric $(C=\tfrac{1}{2})$ alloy CuAu I assuming perfect order $(S=1)$ gave the following values: The energy gap across the (001), (110), (111), and (200) surfaces are 13.8 ev, 12.2 ev, 11.0 ev, and 10.0 ev, respectively. These values are very high. The energy of free electrons at the (001) surface is only 2.4 ev and if the energy gap is indeed 13.8 ev, the electron would be completely confined in the first Brillouin zone and the ordered alloy CuAu I would become an insulator, contrary to experimental data. Consequently, the results based on these calculations seem misleading except for their relative magnitude. Energy gap calculations based on a relation given in Jones' original paper[20] which dealt with the phase boundary based on the Brillouin zone structure are smaller by a factor of π. These values looked slightly more reasonable and have been cited for practical applications of his idea. However, this is due to an error in his expression, and in any case, the calculated values of ΔE_n are much too large.

As Jones already pointed out in his paper, these calculations would give too large a value due to the fact that they are based on the assumption of a point charge for the periodic potential. This is too crude an approximation for slow electrons in metals. In addition, a slow electron cannot penetrate into the ion core and therefore

[27] See for example, N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936).

[28] T. Muto, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 34, 377 (1938).
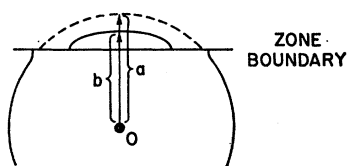
TRUNCATION FACTOR $t = \dfrac{b}{a}$

FIG. 19. Schematic drawing of Fermi surface showing the overlapping of the inner zone boundary.

the total number of electrons of the atom would not contribute to the scattering factor as assumed in calculating the x-ray scattering factor. The free electron can only see the charge of the ion core as a whole, and in this respect the difference in scattering factor between Cu and Au for free electrons in metals would be small. An indirect estimate of the difference in scattering power could be obtained from the resistivity increase of Cu with the addition of Au. It would then be possible to calculate a more realistic value for the energy gaps.[29] A reasonable value of the energy gap based on these ideas is of the order of a fraction of an electron volt.

Since it is now apparent that the energy gap across the Brillouin zone boundaries are much narrower than the calculated value based on Eq. (6), we may assume that the Fermi surface can be approximated by that of free electrons and the electrons overlap freely in the c direction for CuAu I. Therefore, the newly formed energy gap across the {001} boundary would not be important for the present argument. On the other hand, the Fermi surface comes rather close to the {110} boundaries, and therefore the location and the energy gap across this boundary would be very important in determining the behavior of the electrons. When CuAu II is formed, the {110} zone boundaries separate as shown in Fig. 18. Thus, in the case of CuAu II, the Fermi surface is quite close to the *outer* surface of the zone. Now, as the period decreases, the separation of the zone boundaries becomes larger and the outer zone can include more electrons per atom. This tendency agrees quite well qualitatively with the experimental results. Therefore, let us examine this case in more detail.

The volume of the inscribed sphere to the outer zone can be calculated from the separation of the superlattice spots. This is easily found to be

$$V = (\pi/6a^3)(2+2x+x^2)^{\frac{3}{2}}. \qquad (7)$$

Here x represents one-half of the separation of the superlattice spots, and is expressed in terms of the unit reciprocal lattice constant. It is related to the domain size M by the expression

$$x = 1/2M. \qquad (8)$$

The actual shape of the Fermi surface can be considerably distorted from the pure spherical shape because of the existence of the energy gap and also because it

overlaps the inner zone boundary as well as the boundary in the c direction. Therefore, the distance from the origin to the Fermi surface where it touches the outer boundary will be shorter than the radius of the Fermi sphere containing the same number of free electrons. The shape of the Fermi surface to be expected, with respect to the zone boundaries, is shown in Fig. 19. Taking into account the fact that there are four atoms per unit cell, the number of electrons per atom, e/a, which will be included in this surface is given by

$$e/a = (\pi/12t^3)(2+2x+x^2)^{\frac{3}{2}}, \qquad (9)$$

where t is a truncation factor which gives the measure of the nonsphericity of the Fermi surface and its definition is indicated in Fig. 19. Although this factor is expected to change as the zone boundary separation changes, one can expect it to be approximately constant over a limited range. Since this factor is difficult to calculate quantitatively, let us take this factor as an adjustable parameter and determine its value at a known point or from the best fit to the experimental results. Such a fixed point is stoichiometric CuAu II, where $M = 5.0$ and the electron-atom ratio is one. The calculations show the value of t thus determined to be 0.95, which is a reasonable number. However, the determined value of t may also include the effect of other energy terms such as the domain boundary energy (cf. Sec. V.B) which also affects the period along with the kinetic energy of free electrons.

Utilizing Eqs. (8) and (9), the relation between e/a and M was calculated and compared with the experimental results. This is shown in Fig. 20. As can be seen, the agreement is very good. In addition, a further calc-
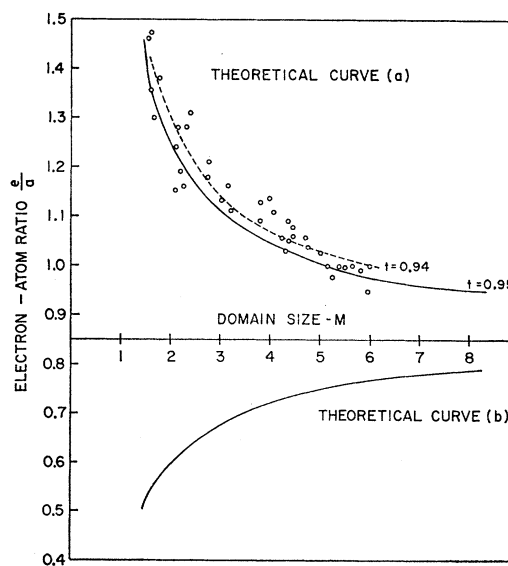

FIG. 20. Theoretical curve of electron-atom ratio vs domain size M with $t = 0.95$ for (a) stabilization by outer Brillouin zone and showing its relation to the experimental points for CuAu II and (b) stabilization by inner zone boundary. The dotted line shows the curve for $t = 0.94$.

[29] See for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940).

ulation shows that M becomes infinite at $e/a=0.86$, which agrees almost exactly with the value obtained by linear extrapolation of the experimental curve in Fig. 16. Although the agreement is satisfactory, $t=0.94$ seems to give a better fit at larger e/a values. This systematic discrepancy may be explained as a result of the boundary energy mentioned above or a systematic deficiency of the third elements as compared to the computed values.

The good agreement between the theoretical values and experimental data along with a reasonable value of the adjustable parameter t supports our conclusion that the stabilization due to the splitting of the Brillouin zone is the essential factor for forming the CuAu II structure.

The agreement between the theoretical predictions and the experimental data is not limited only to the Cu-Au system. In other systems where one dimensional long periodic structures are found, the agreement is equally good. For example, in the Ag-Mg system near Ag_3Mg, the dependence of the domain size on the electron-atom ratio is also given by Eq. (9) with a similar truncation factor.

If the electron-atom ratio is smaller than the critical value (0.86 for CuAu II for example), the stabilization of the alloy should take place by the relation between the Fermi surface and the inner zone boundary contrary to the previous case where the relation between the Fermi surface and the outer zone determines the domain size. In such a case, using the same argument as before, the relation between the domain size and the electron-atom ratio is also given in terms of the separation value x, by the equation

$$e/a= (\pi/12t^3)(2-2x+x^2)^{\frac{3}{2}}. \qquad (10)$$

The curve obtained from this relation is shown in Fig. 20. In this case, the domain size decreases with the decrease of the electron-atom ratio. In the case of the one-dimensional periodic superlattice found in the Cu-Pd system around 20% Pd, the domain size is accurately predicted by Eq. (10), using a truncation factor similar to that obtained for the Cu-Au system. In general, predictions concerning the behavior for cases where the electron-atom ratio is smaller than the critical value are just reversed from those for the cases where e/a is greater than this value.

The theory not only predicts the variation of the domain size with the electron-atom ratio, but also predicts other characteristics of the long period superlattices which are in accord with experimental results. For example, we may discuss the distortion of the crystal when it forms the long period structure. So far, we considered only the reduction in the kinetic energy of free electrons for a fixed crystal when the extra period is introduced. Although this is enough to predict the period to a first approximation, the true value would be determined from the minimum of the sum of the energy terms which depend upon the formation of the antiphase

domains allowing also the deformation of the crystal. These energy terms would be, in addition to the kinetic energy of free electrons, the antiphase domain boundary energy (out of step boundary energy), the elastic energy, etc. The distortion of the lattice can be discussed along this line. Let us first discuss the case when the electron-atom ratio is greater than the critical value as in the case of CuAu II. In such a case, the Fermi sphere overlaps at the inner zone boundary and touches the outer zone boundary, and the Fermi surface is inside the outer zone boundary. Under such a condition, it is known that the Fermi surface has a tendency to pull in the outer zone boundary toward it in order to increase the stabilization.[30] At the same time, the overlapped portion of the electrons across the inner zone boundary has a tendency to push the inner zone up so that the number of overlapped electrons would decrease although the main effect would be the former one. Both tendencies can be achieved by a distortion of the Brillouin zone in such a manner that the zone is compressed in the direction of the period. This, in turn, means that the crystal lattice has a tendency to elongate in the direction of the period. This explains the fact that CuAu II elongates in the b direction. Ag-Mg alloys near the composition of Ag_3Mg or Au-Cd alloys near Au_3Cd, where a one dimensional long period sturcture is formed in the c direction, follow the same tendency, and c/a becomes larger than one.[31] There is, at the same time, a tendency that a small overlap of electrons across the boundary planes of the inner Brillouin zones causes an internal stress in the crystal which tends to squeeze the Brillouin zone in a direction at right angles to the overlapped plane.[20] This stress, however, is balanced by the similar overlap in the other directions and would not cause an extra distortion except for the AuCu II type structure where the Brillouin zone structure is anisotropic. If, on the other hand, the electron-atom ratio is smaller than the critical value, the stabilization takes place at the inner zone instead of the outer zone. Just as in the previous case, the Fermi surface has a tendency to pull in the inner zone. This can be achieved by the elongation of the Brillouin zone in the c direction. In other words in such an alloy, there is a tendency that the lattice contracts in the direction of the period. This is exactly the case for Cu-Pd alloys around 20% Pd. An important feature in both cases is that the Fermi surface should not overlap across the zone boundary where the stabilization takes place.

The distortion of the lattice takes place mainly at the expense of the elastic energy and the actual amount would be determined by the balance of the two energy terms.

[30] J. B. Goodenough, Phys. Rev. **89**, 282 (1953).

[31] In the case of CuAu II, the alloy is originally tetragonal with $c/a=0.92$, and therefore the distortion we are talking about occurs in the b-direction as already pointed out. In the case of Ag-Mg and Cu-Pd alloys, however, the alloys are originally cubic and therefore they distort tetragonally when they form the long period superlattice.

In the former case, the distortion takes place in the direction to increase x at a fixed value of the electron-atom ratio. In this sense, the distortion takes place also at the expense of the domain boundary energy because a larger x corresponds to a shorter period and, therefore an increased number of domain boundaries. However, the tendency to make the total number of overlap of electrons smaller during the deformation tends to counterbalance this effect. In the latter case, however, the distortion is in the direction of decreasing x at a fixed value of the electron-atom ratio. Therefore, the domain boundary energy aids the distortion. The contribution of the domain boundary energy to this problem, however, is expected to be much less than the elastic energy.

Thus far, our model explains in a very convincing way the characteristics found in alloy systems with long-period superlattices. In this sense, another implication of the present theory might be the added strong support of Jones' initial model explaining the phase boundary of alloys.[20] According to his model, the phase boundary occurs at the e/a concentration where the Fermi surface just touches the Brillouin zone. This idea has been applied in many places and has attained a great deal of success.[32] However, the recent study on the Fermi surface of precious metals (Cu, Au, Ag) by the measurement of the de Haas–van Alphen effect, the anomalous skin effect, and other effects, indicates that the Fermi surface already touches the {111} surface of the Brillouin zone. This fact casts doubt on the validity of Jones' original idea, for if the Fermi surface touches the Brillouin zone boundary from the beginning, his arguments have no basis. However, the continuous change of the domain size with the number of electrons of the long-period superlattice as well as the distortion of the crystal can most conveniently be explained from the idea that the Brillouin zone boundary just touches and moves with the Fermi surface. Therefore it is desirable that the relation between the idea about the stabilization of an alloy phase at the Brillouin zone boundary and the conclusion that the Fermi surface of pure elements Cu, Ag, Au, etc. touches the zone boundary should be investigated in more detail.[33]

B. Concentration and Temperature Effect

If the composition of the alloy changes from the stoichiometric ratio, CuAu, the period increases. This effect cannot be explained by the change of the electron-atom ratio, as explained above and we shall call this effect the concentration effect. The concentration effect may be explained mainly as the effect of the domain boundary energy in the following way. When the con-

centration is changed from the stoichiometric composition, the energy for stabilization at a definite period becomes shallower without changing the position of the minimum, and the decrease would be linear with the change in the concentration. This effect can be understood easily from the expression for the energy gap, Eq. (6). At the same time, the domain boundary energy increases with the number of boundaries and, therefore, is a monotonic function of $1/M$. Therefore, if these energy terms are added, the minimum is shifted to the direction of the longer period from the value given in Eq. (9) where only the energy of the free electrons is taken into account. This shift is larger as the minimum becomes shallower. Thus, as the composition of CuAu departs more and more from stoichiometry, the minimum shifts to larger values of the period, in accord with the experimental data. This explains the concentration dependence of the period as well as the effect of the addition of Ag to CuAu II. This effect should exist at any concentration and in any alloy. Therefore, the true period found in alloys would be somewhat larger than the period predicted by Eq. (9). Due to the difficulty of calculating quantitatively the energy stabilization and the domain boundary energy, it is difficult to make a quantitative calculation of this effect.

The question of whether a long-period superlattice can exist or not also depends on the relative magnitudes of the energy of stabilization due to splitting of the Brillouin zone and of the increase in domain boundary energy to create the antiphase domains. In the Cu-Au alloy, it seems that the condition is critical, and this can be envisaged from the fact that the concentration effect is large. By lowering the temperature, the increase in domain boundary energy overcomes the stabilization energy, and the CuAu II structure transforms into the CuAu I type. Although both energy terms will increase in magnitude by lowering the temperature, the domain boundary energy should have a stronger temperature dependence. The fact that the difference in magnitude between the energy of stabilization and the domain boundary energy is not much thus explains the concentration and the temperature dependence of the Cu-Au system. The reason why the long-period superlattice is not stabilized in the Cu_3Au region would also be explained from this viewpoint.

The explanation thus far indicates that the long-period superlattice is actually the most stable state for the ordered alloy, and therefore all ordered alloys should form long-period superlattices instead of the regular ones. However, as is indicated above, the relative magnitude of the domain boundary energy with respect to the stabilization energy mainly determines the situation whether the long-period structure is the most stable state or not. Actually, if the long-period superlattice is once stabilized, it remains as the stable state to the lowest temperatures except for the case of CuAu II. Another indirect support of the importance of the domain boundary energy follows from the fact that we

[32] See for example, G. V. Raynor, *Progress in Metal Physics* (Butterworth Scientific Publications, London, 1949), Vol. 1, p. 1; T. B. Massalski, *Theory of Alloy Phases* (American Society for Metals, Cleveland, Ohio, 1956), p. 63.

[33] Some arguments concerning this point can be found in M. H. Cohen and V. Heine, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1958), Vol. 7, p. 395.

usually do not find alloys with very long periods. In other words, the alloys seem to take the value $M = \infty$ (the regular superlattice) when the theory predicts a very large value for M. If the period is long, the separation of the Brillouin zone becomes extremely small, and the alloy does not gain enough energy for the stabilization to form a long period structure and this is easily overcome by the domain boundary energy. However, it may be rather hard to check this point experimentally.

The relative importance of the domain boundary energy with respect to the energy of the stabilization in CuAu indicates also that the main cause for the formation of the ordered structure of this alloy would still be a short-range interaction energy between the different kinds of pairs of atoms, since the main contribution to the domain boundary energy is due to the short-range interaction by the creation of wrong atom pairs at the boundary. The situation for the other alloy systems would in general be similar to the Cu-Au alloy and it would be safe to say that the origin of the formation of ordinary type superlattices such as CuAu I, Cu_3Au, etc. would mainly be the conventional short-range interaction and not the stabilization due to the splitting of the Brillouin zone as suggested by Nicholas[21] except for special cases. The relative importance of the Brillouin zone stabilization and the short-range interaction, however, depends very sensitively on the kind of constituent atoms.

VI. CONCLUSION

The experimental data obtained in this research indicated that the number of free electrons in the system is the deciding factor for the stabilization of long-period superlattices.

From this information, a theoretical model based on the Brillouin zone was adopted for explaining the origin of the stabilization of such a long period structure. It was found that the theory not only predicts the domain size dependence upon the electron-atom ratio, which agrees satisfactorily with the experimental results obtained, but also it explains all other characteristics of CuAu II, if the domain boundary energy is properly taken into account.

As briefly indicated in the text, the theory explains the characteristics of other long-period superlattices as well. In this respect, we can legitimately say that the enigma concerning the origin of the formation of long-period superlattices has been solved. A detailed discussion on the application of the present theory to other alloy systems and to characteristics not found in CuAu II will be given in another paper.
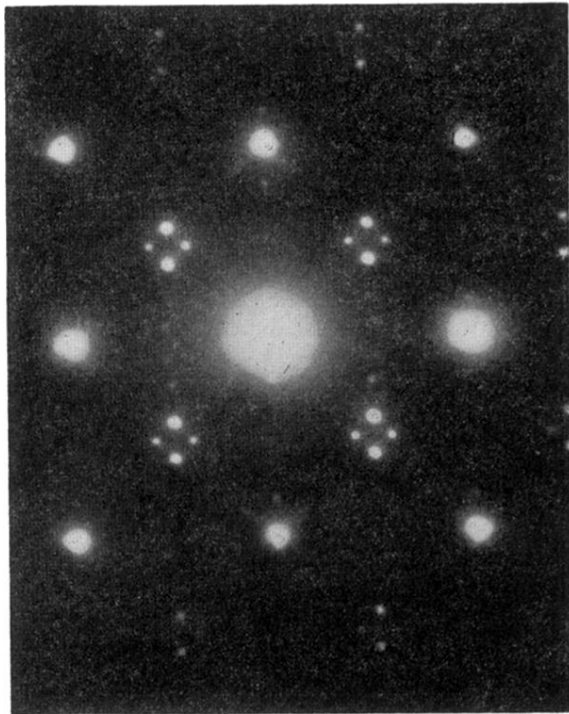
ACKNOWLEDGMENTS

FIG. 11. Electron diffraction pattern of CuAu II containing 5.8%
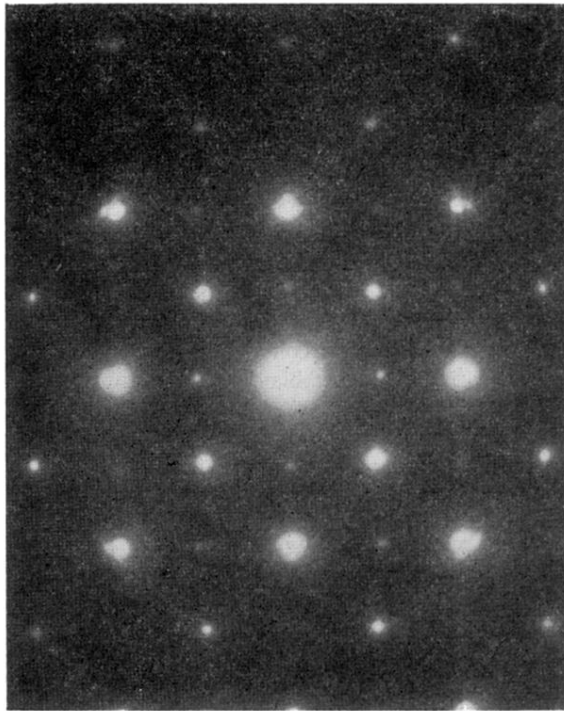Al showing increased separation of superlattice spots.

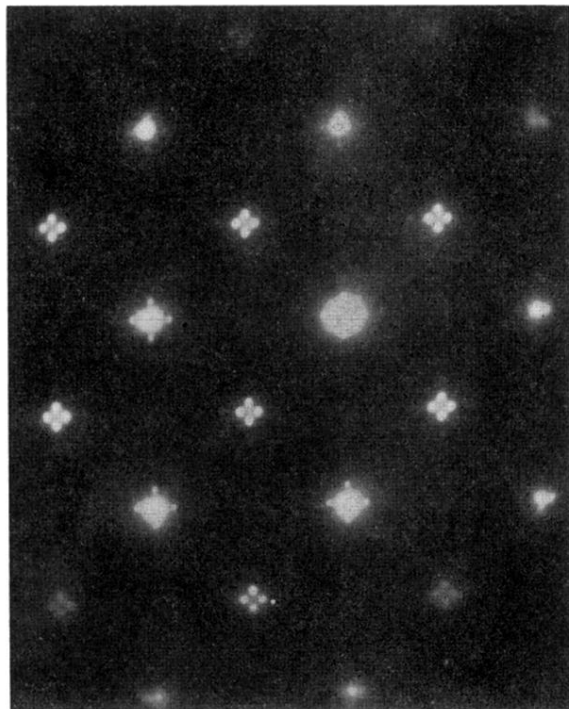FIG. 3. Electron diffraction pattern of CuAu I.

Fig. 4. Electron diffraction pattern of stoichiometric CuAu II.

FIG. 5. Electron micrograph of CuAu II showing antiphase
domain structure. Magnification 320 000 ×.