(Abstand Cu–O, bzw. OH, H_2O = 1,9 bis 2,0 Å) mit Ergänzung durch zwei weitere Nachbarn (vgl. Orgel & Dunitz, 1957, und Wells, 1949) im Abstande von 2,2 bis 2,5 Å zu einem verzerrten Oktaeder. Das wurde vor kurzem von Kokkoros & Rentzeperis (1958) auch für das farblose $CuSO_4$ gezeigt. Bei den gut belegten Strukturen von dunkelblauen Cu^{2+}-Salzen ($[Cu(NH_3)_4]SO_4.H_2O$: Simerská (1954), Mazzi (1955); $Cu_2Mg_2CO_3(OH)_6.2\,H_2O$: Brunton et al. (1958); $CuSeO_3.2\,H_2O$: Gattow (1958); $Cu_3(OH)_2(CO_3)_2$: vorliegende Arbeit) ist mindestens einer der Nachbarn ausserhalb der planar-quadratischen Koordination deutlich weiter entfernt, bzw. eine 'oktaedrische' Umgebung ist kaum mehr erkennbar (Cu_I im Azurit). Auf Grund des vorliegenden Untersuchungsmaterials ist zu erwarten, dass dieses eine allgemeine Erscheinung in der Kristallchemie von dunkelblauen Cu^{2+}-Verbindungen ist. Zu ähnlichen Ergebnissen für dunkelblaue Cu^{2+}-Komplexe in Lösungen kamen Bjerrum et al. (1954) bei der Diskussion der Absorptionsspektra.

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The Direct Observation of the Long Period of the Ordered Alloy CuAu(II) by Means of Electron Microscope

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Using thin evaporated films, the ordered structure of CuAu(II) with long period has been studied by means of the transmission electron microscope. Parallel lines spaced at intervals of about 20 Å have been observed, corresponding to satellite spots flanking the direct spot in the diffraction pattern. Their spacing is in close agreement with the size of an anti-phase domain. The lines are believed to be caused by some lattice modulation with the same period as the domain size, the possibility of moiré pattern based on secondary diffraction being disputed. By a careful examination of the spacing of the lines the existence of different domain sizes previously concluded from diffraction maxima has been proved and a mode of mixture of them has been shown.

1. Introduction

According to the electron diffraction studies on ordered alloys such as CuAu(II) (Ogawa & Watanabe, 1954), Cu_3Pt (Watanabe, 1955), Ag_3Mg (Fujiwara, Hirabayashi, Watanabe & Ogawa, 1958), Cu_3Pd (Watanabe & Ogawa, 1956), Au_3Mn (Ogawa & Watanabe, 1957), Au_4Zn and Au_3Zn (Fujiwara, Watanabe & Ogawa, 1957), it was revealed that they possess superlattices consisting of anti-phase domains with definite size in a stable state. For example, CuAu(II) has a one-dimensional anti-phase domain structure characterized by the first kind of out-of-step,

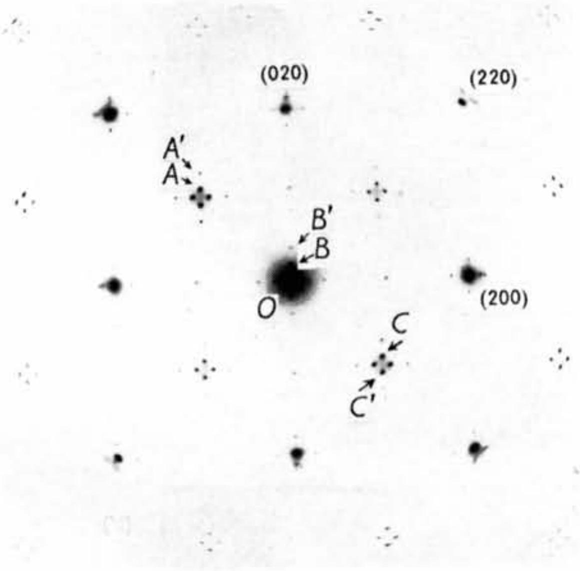

Fig. 2. Electron diffraction pattern of CuAu(II); normal incidence.

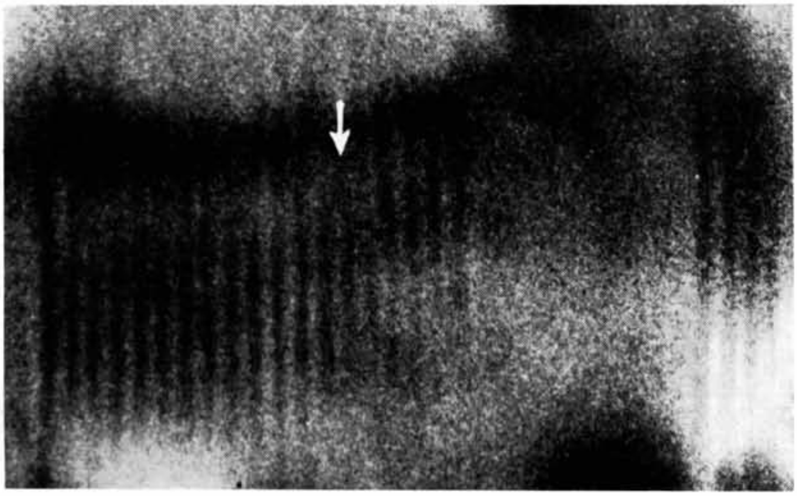

Fig. 3(*a*). Electron micrograph of CuAu(II) film (1,500,000×).

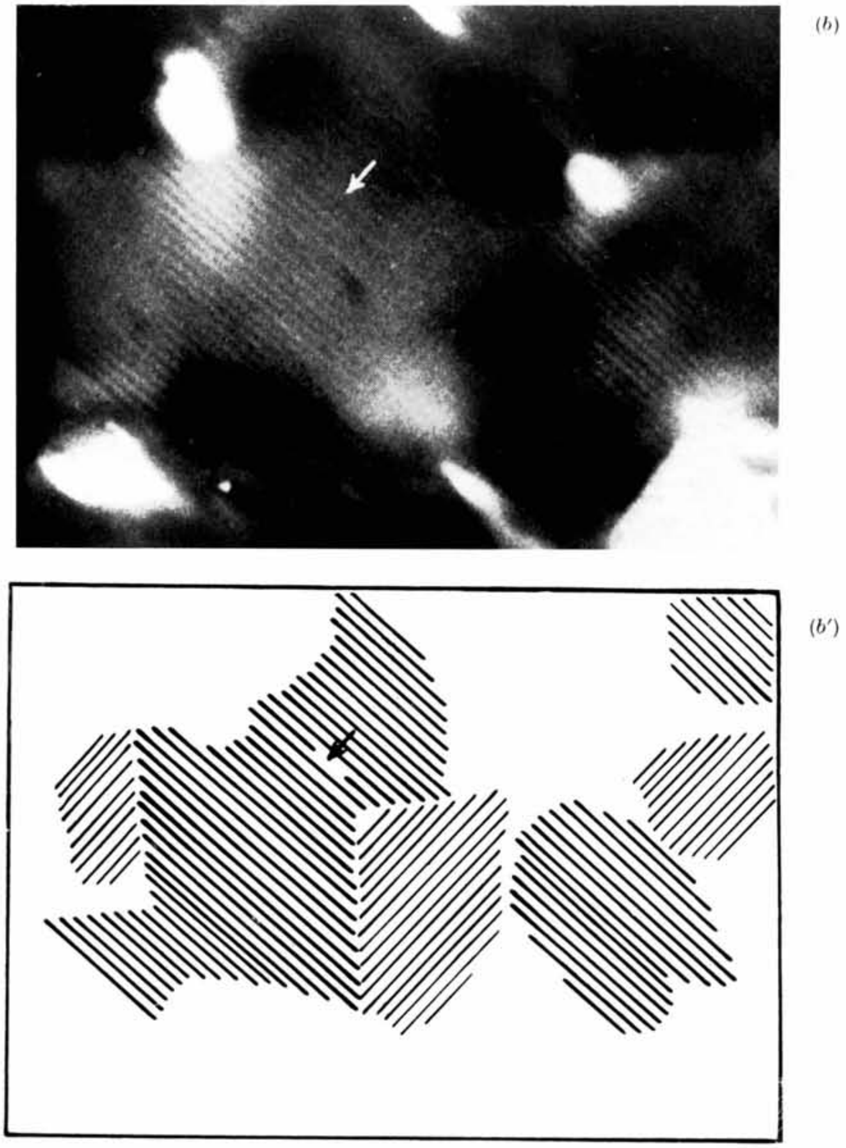

Fig. 3(*b*). Electron micrograph of CuAu(II) film (720,000×).
(*b*′) is an illustration of (*b*).

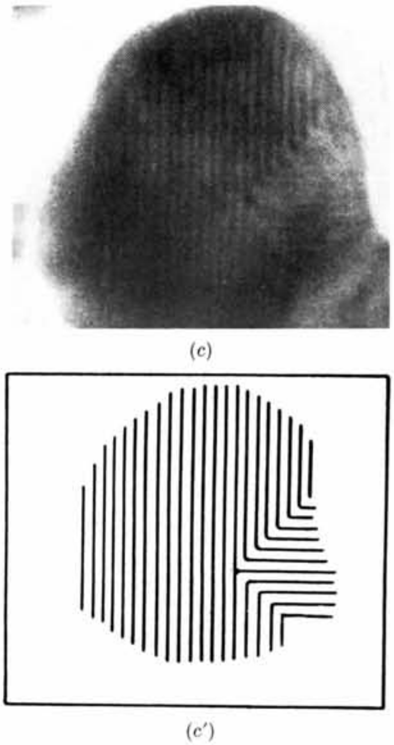

Fig. 3(*c*). Electron micrograph of CuAu(II) film (720,000×).
(*c*′) is an illustrations of (*c*).

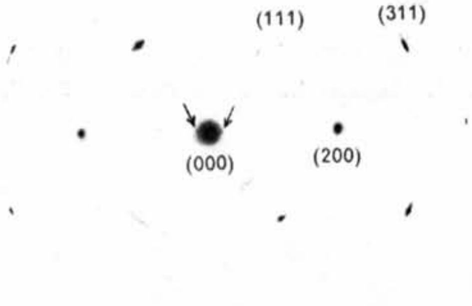

Fig. 4. Electron diffraction pattern of the same film as in Fig. 2; {110} incidence.
Arrows indicate the residual satellites around the direct spot.

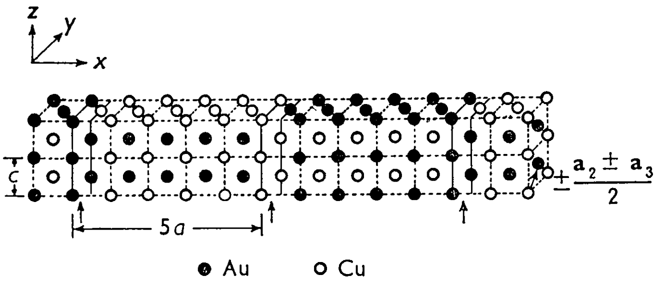

Fig. 1. The ordered structure of CuAu(II). Out-of-steps $\pm(\mathbf{a}_2 \pm \mathbf{a}_3)/2$ occur at places indicated by arrows.

as shown in Fig. 1, while Cu_3Pd has a two-dimensional anti-phase domain structure characterized by combination of the first kind and the second kind of out-of-step.

Fig. 2 shows an electron diffraction pattern obtained from a single-crystalline, evaporated film of CuAu(II). Cross-like splits at superlattice reflection positions indicate the occurrence of line-up of anti-phase domains in the crystal lattice. On the other hand, satellites flanking main reflections, which are most conspicuous around the direct spot and clearly visible even to the third order on the original plate, cannot be derived from the simple line-up of anti-phase domains. Their origin is not yet thoroughly clear, but we can assume that some kind of periodic modulation in the ordered lattice may cause them to appear just as a periodic error of an optical grating gives rise to a so-called ghost. The similar satellites were observed in the other alloys except for Cu_3Pt and Ag_3Mg. The period of the modulation estimated from separations of the satellites from the relevant main reflections always coincides with a length of the anti-phase domain concerned, i.e., a period of out-of-step. Thus, the existence of the satellites means some periodic modulation to accompany anti-phase domains, whether it may suggest a periodic error of lattice spacing or of scattering factor.

Recently, the transmission electron microscope has been greatly improved in its resolving power, and Menter (1956) could resolve some crystal lattice planes of copper and platinum phthalocyanine, using thin films. The distance between the $(20\bar{1})$ planes of platinum phthalocyanine (12·0±0·2 Å) observed on electron micrographs was in close agreement with the X-ray value of 11·94 Å. Since the length of each anti-phase domain of CuAu(II), being five times the lattice constant of the fundamental lattice, is about 20 Å, we may anticipate that the periodic modulation as presumed above may be directly observed by means of an electron microscope of high quality, utilizing the satellites flanking the direct spot to image formation. The present authors have in fact succeeded in obtaining distinct images of parallel lines having the expected spacing on the electron micrographs of CuAu(II) films, as described in Section 3.

2. Experimental

Specimen films were prepared as follows: Gold was initially evaporated *in vacuo* on to the cleavage surfaces of rock-salt heated at 400 °C., and copper was then successively evaporated on to them at room temperature. Thus, single-crystalline composite films with (001) orientation were formed. After having been detached from the substrates and mounted on thin collodion films set on platinum meshes or titanium plates with pin holes, the films were heated *in vacuo* at 400–420 °C. for 2 hrs. for alloying and ordering. The quantity of each component of metal was adjusted so that the atomic ratio became 1 to 1. The composition of the alloy films was determined from measured lattice constants. It was desirable that the thickness of the alloy films was diminished as much as possible from a viewpoint of transmission electron microscopy, but there was a limit caused by breakdown of films; the smallest thickness attained was about 250 Å.

The electron microscope used was of the HU-10 type produced by Hitachi Company, and was operated at 75 kV. The focal length of the objective lens was 3 mm. and the aperture size was 50 $\mu\phi$. The images were recorded on Fuji Process plates (hard) at a magnification of 100,000–120,000×.

3. Results

The electron micrographs shown in Figs. 3(*a*), (*b*) and (*c*) exhibit the structure of CuAu(II) films, corresponding to the diffraction pattern in Fig. 2. The maximum scattering angle limited by the objective aperture could cover up to the neighborhood of {100}[*] superlattice reflections. These electron micrographs are of very high magnification and reveal regularly spaced parallel lines. Their spacing was roughly estimated to be 20 Å, although there was some fluctuation.

The lattice constants of the present alloy in terms of the fundamental tetragonal lattice are: $a = 3{\cdot}96$ Å, $c/a = 0{\cdot}93$. The composition determined from the lattice constants deviated somewhat from 1 to 1 and corresponds to 45 atomic per cent copper. In the case of CuAu(II) the domain size measured in a M, equals 5 at 1 to 1 composition, but increases as the composition deviates from the stoichiometric value and is in general not an integer (Watanabe & Ogawa, 1956). It is 5·4 in the present composition. Ma equals 21·4 Å which nearly matches the spacing of the lines in question. This coincidence indicates that the parallel lines are directly related to the anti-phase domain structure. Therefore, we may be able to say that we have the first direct observation of some lattice period in metals and alloys by the present electron micrographs.

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[*] The Miller indices are used here in terms of the original disordered cubic lattice.

The electron microscopic observation as above can be applied to study the distribution of anti-phase domains in the films. So far as our observations were concerned, the area covered by the parallel lines were about 500 Å on one side and from 500 to 1000 Å on the other side. In Fig. 3(*b*), a set of faint lines orthogonal to a set of strong lines can be seen. Since the parallel lines should be perpendicular to the line-up direction of anti-phase domains, it is clear that the two perpendicular directions correspond to two cubic axes of the original disordered lattice along which anti-phase domains of the ordered lattice have been lined up. The boundary of the perpendicular sets is more clearly observable in Fig. 3(*c*) and (*c*′) and is parallel to {110} indexed in terms of the original lattice. Some irregularities are seen in the arrangement of the parallel lines, e.g., in places indicated by arrows in Figs. 3(*a*) and (*b*). They may be of significance, just as Menter (1956) ascribed similar imperfections in his observation to an indication of dislocations of the crystal lattice. However, a hasty conclusion concerning the imperfections should not be made in the present case, since, according to Hashimoto (1958), similar imperfections observed on microscopical images of a grating are often caused by a slight amount of dirt in an irradiating system or by slight defocusing.

4. Discussion

Though we presumed in Section 1 that the satellites flanking the direct spot are due to the modulation of the ordered lattice, there is another possible explanation that the satellites are caused by secondary diffraction of crosses at {110} superlattice reflection positions. If the present alloy film was a superposition of the two incoherent layers which, however, possessed the same line-up direction of anti-phase domains, the satellites might be formed as follows: For example, an electron beam causing a diffraction spot, *A*, in a cross in Fig. 2 gives rise to a pair of split, *B* and *O*, at the center of the pattern by secondary diffraction, just like the central beam at *O* gives rise to a pair of split, *C* and *C*′, by primary diffraction due to the line-up of anti-phase domains. Through similar processes all of the satellites flanking the direct spot might be formed.

If this explanation were the case, the lines shown in Fig. 3 should be interpreted as moiré patterns caused by reflections from the lattice planes with smaller spacings corresponding to split spots of the crosses, and then the lines should not be regarded as a direct image of the crystal lattice. However, the present authors consider that a greater part of intensity of the satellites is due to the periodic modulation of the lattice, as already mentioned, but not to the secondary diffraction, from the following three reasons:

(i) The satellites are too strong in intensity to arise from secondary diffraction. In general, their intensities are almost the same in the order of magnitude as those of splits in superlattice reflections (compare *A* and *A*′ with *B* and *B*′, respectively), while this fact is very difficult to explain according to the process in question.

(ii) If secondary diffraction played an important rôle, the satellites around the direct spot should not appear when the crosses disappear. Fig. 4 shows a pattern obtained when the film plane was inclined to the beam by 45° around a direction parallel to one of the original cubic axes, and therefore the pattern closely approximates to the intensity distribution in a {110} section of reciprocal space. The crosses seen in Fig. 2 disappear now, since they are located at face-centred positions in reciprocal space. Some of the satellites are, nevertheless, clearly visible around the direct spot. That is to say, those which are situated along the reciprocal axis parallel to the rotating axis remain after the inclination of the film. This result shows that the satellites are not formed by secondary diffraction but due to the points which originally exist in reciprocal space. This fact is the most striking disproof against the process of secondary diffraction and has been confirmed also in the case of Au_3Mn.

(iii) Although secondary diffraction is hardly conceivable to take place in the case of X-ray diffraction, Wilkens & Schubert (1957) have succeeded in observing satellites of the same kind as in the present case by X-rays in a powdered specimen of Cu_{50} Au_{20} Zn_{30} which has a two-dimensional anti-phase domain structure similar to Au_3Mn (Ogawa & Watanabe, 1957). This fact stands against the explanation based on secondary diffraction, too.

After the above-mentioned three experimental evidences, we can conclude that the satellites in question are undoubtedly caused by the periodic modulation of the lattice. Though there are certain evidences of secondary diffraction in some cases as confirmed for a CuAu(II) film (Ogawa & Watanabe, 1954), its effect on the intensity of the satellites will be only slight and it may be neglected when the nature of these is investigated.

As described in Section 3, the number *M* indicating the size of an anti-phase domain, estimated from separations of split maxima, is in general a fractional number, which means a mixture of different domain sizes in a coherent crystal lattice. In the present case, *M* equals 5·4, and therefore, it is conceived that a line-up of anti-phase domains contains two kinds of *M* value, 5 and 6. Since the parallel lines seen in Fig. 3 correspond to a Fourier projection of the lattice based on the satellites flanking the direct spot, they must involve an information on mixture of domains of different sizes. Fig. 5 shows the distribution of the distances between the lines obtained by measuring about one hundred distances. There appear two peaks at 19 Å and 23 Å in the figure which nearly correspond to $M = 4{\cdot}8$ and 5·8 respectively. Considering some systematic error involved in the estimation of magnification, the two peaks are considered to correspond to the integral *M* values 5 and 6, respectively.

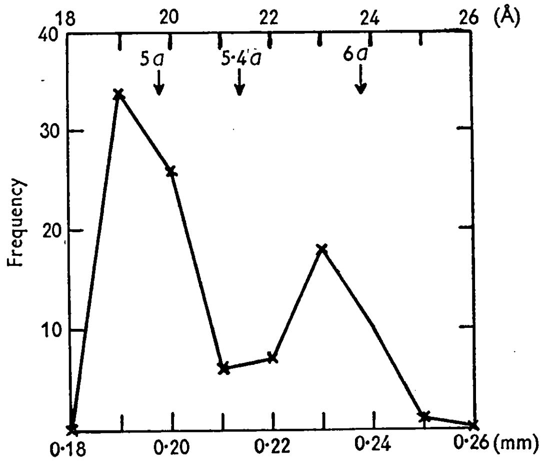

Fig. 5. Relation between the line distance and its frequency

It is very interesting to examine whether a mode of mixture of the two kinds of anti-phase domain is regular or irregular. As Fujiwara (1957) showed, a uniform irregular mixture and a uniform regular mixture yield a similar intensity distribution of diffraction. Thus the discrimination between them is very difficult to detect by a diffraction pattern. The mode of mixture, however, can be directly observed on electron micrographs. Examples of the observed mode of mixture are shown in terms of *M*, as follows:

...6555656655655556555655...
...565565556565... ,

where the measured domain size is classified into either of the two kinds, the experimental error being considered. The mixture in other parts was also almost similar to the above. That is to say, a uniform irregular mode of mixture seems to be substantially realized. Of course, a sufficiently large number of distances between the lines should be examined in various ordered alloy films with anti-phase domains, before a definite conclusion is drawn from such observations. So far as we have observed in a CuAu(II) film, however, the mode of mixture of anti-phase domains seems to be characterized by its uniformity but not by regularity, as concluded previously by Fujiwara (1957).

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The Crystal and Molecular Structure of Diformylhydrazine, OHC–HN–NH–CHO. II. On the Electronic Structure of the Molecule

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The electronic structure of the diformylhydrazine molecule has been investigated by the use of a simple *MO* method. Calculated values of the number of π-electrons, the charge and the total number of electrons associated with each atom (in which the σ-bond correction is made) are reasonable in comparison with those observed by the X-ray Fourier series method. In obtaining calculated heteropolar bond lengths, a correction term due to the charges has been introduced to the order-length relation of a bond, as the atoms in the molecule have large charges. The resonance structures and the fractional double bond characters of *VB* type have been discussed also. For the determination of the energy levels, non-orthogonality of the *AO*'s between adjacent atoms has been considered. The predominant factor contributing to the stability of the planar structure is the charge effect. The energy of conjugation between the two –HNCHO groups in the molecule does not exceed 4 kcal.mole^{-1}. Assignment of the near ultra-violet absorption spectra of the molecule in the crystal has been carried out group-theoretically using the results of the *MO* calculation and thus the existence of conjugation in this molecule has also been proved spectroscopically.

Introduction

In the crystal structure of diformylhydrazine (as determined by Tomiie, Koo & Nitta (1958), hereafter called (I)) the molecule has a planar S shape with