étudiées: volume moyen offert à chaque particule, température et potentiel $\Phi(r)$ des forces interparticulaires. Les principaux avantages que présentent donc cette formula sont:

(1) Sans connaitre $\Phi(r)$ elle permet de prévoir les modifications qu'apporte à la courbe de diffusion le rapprochement des particules.

(2) Si on connait le potentiel $\Phi(r)$ on peut calculer les courbes de diffusion relatives à toutes les concentrations de la matière et toutes les températures.

(3) Si on dispose de plusieurs courbes de diffusion relatives à un gaz plus ou moins comprimé (ou une solution de grosses particules plus ou moins étendue) on peut déterminer le potentiel des forces interparticulaires.

Nous croyons que le développement de ces méthodes est susceptible d'apporter d'utiles renseignements sur la microstructure de la matière.

Ce travail a été exécuté, au Conservatoire National des Arts et Métiers, dans le Laboratoire du Prof. Guinier. Nous sommes heureux de remercier Monsieur le Prof. Guinier pour l'intérêt qu'il a porté à ce travail.

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Modulated Structures in Some Copper–Nickel–Iron Alloys

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Some copper–nickel–iron alloys, of compositions characterized by the occurrence of a modulated structure as a pre-precipitation stage in the transformation of the single-phase cubic to the two-phase cubic structure, have been re-examined by means of a refined technique which permits X-ray diffraction patterns of powder specimens to be made using only the $K\alpha_1$ characteristic radiation. X-ray patterns of single crystals and microscopic examination of lump specimens have also been employed.

The experimental results are described and compared with the theory of diffraction for a modulated lattice, to which some extensions are made. The modulated structure is considered to be composed of a regular arrangement of coherent lamellae of two intermediate tetragonal phases, and the wave form of the modulation assumed is rectangular. Excellent agreement between theory and experiment is obtained over the range of existence of the modulated structure.

The relation between the diffraction patterns of the modulated structures and those which arise from independent particles of the intermediate phases is discussed, and the possible relevance of this relation to the interpretation of the diffraction patterns of alloys of the age-hardening type is indicated.

1. Introduction

This paper is concerned with alloys lying in the field marked 'metastable states' in the phase diagram (due to Bradley, Cox & Goldschmidt, 1941) for slowly cooled Cu–Ni–Fe alloys (Fig. 1). This field lies at the extremity of the solid solubility gap in the face-centred cubic solid solution, and in it the tie lines correspond to approximately constant Ni:Fe ratios, so that the separation of the two equilibrium (face-centred cubic) phases involves, chiefly, the diffusion of copper atoms.

Bradley (1940) showed that during the annealing of quenched single-phase alloys in this field, two intermediate tetragonal phases appeared—prior to the

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separation of the cubic equilibrium phases—both having the same a dimension as the quenched alloy, but with axial ratios c/a slightly greater than, and slightly less than, unity. It was assumed that the two tetragonal phases are conjugate, one Cu-rich ($c/a > 1$), the other Cu-poor ($c/a < 1$), corresponding to the conjugate cubic phases of the equilibrium state.

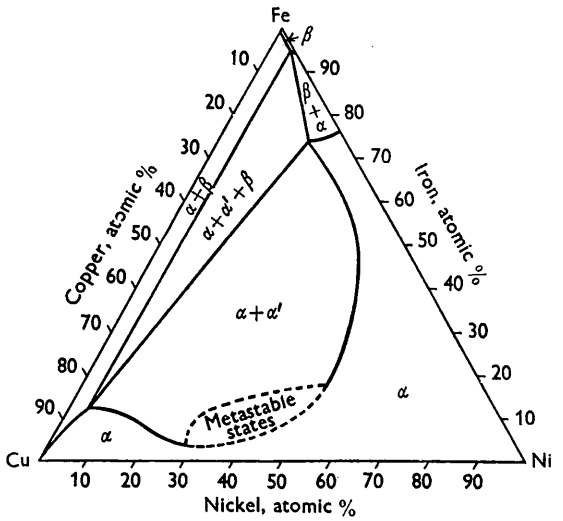


Fig. 1. The copper–nickel–iron system according to Bradley *et al.* (1941, Fig. 4). (Reproduced by permission from the *Journal of the Institute of Metals*.)

The powder patterns of alloys annealed for periods too short to produce the tetragonal phases showed 'side-bands' accompanying the lines of the single-phase structure, and Daniel & Lipson (1943, 1944) concluded that the anomalous diffraction effects could be accounted for on the assumption that the lattice parameter is modulated in the directions of the cube axes. The observed positions of the side-bands were in excellent agreement with the theory of the modulated structure, but the observed intensities of the side-bands, relative to those of the corresponding main lines, could not be explained without the application of a large and somewhat arbitrary correction for extinction.

The present paper describes a further experimental study of the modulated structures. In §2 we give some extensions to the theory of diffraction by a modulated lattice, required for the interpretation of the experimental results set out in §4 and discussed in §5. The experimental technique is described in §3.

2. Theoretical

(a) *Previous theoretical treatments*

Daniel & Lipson (1943, 1944) showed that the diffraction from a one-dimensional grating, modulated sinusoidally, consists of the main reflexions of the unmodulated grating, with satellite reflexions, having intensities governed by the following relations:

(i) *Modulation of scattering power.* The main reflexion, i.e. integral order of diffraction h of amplitude unity, is accompanied by a pair of satellite reflexions of orders $h \pm 1/Q$ and of amplitude $\frac{1}{2}A$, where A is the amplitude of the modulation of scattering power, and Q its wave-length expressed as a number of unit cells (grating spacings). The amplitude of the satellites is thus independent of the order of the main reflexion.

(ii) *Modulation of spacing.* The main reflexion of order h, amplitude $J_0(hQb/a)$, is accompanied by pairs of satellites of order $h \pm p/Q$, amplitudes $J_p(hQb/a)$, where J_p is the Bessel function of the first kind of order p (p being a small integer), and b and Q are the amplitude and wave-length of the modulation of the original spacing a. The amplitude of the satellites thus depends upon the order of the main reflexion, and, in particular, is zero if h is zero. The amplitude of the satellites decreases rapidly as p, the order of the satellites,* increases.

Preston (1938) calculated the effects due to simultaneous modulations of scattering power and spacing; a more exact calculation (Hargreaves, 1949), using the methods and notation of Daniel & Lipson, shows that the main reflexion of order h, amplitude $J_0(hQb/a)$, is accompanied by satellites of order $h - 1/Q$ of amplitude

$$\frac{A}{2}J_0\left(\frac{hQb}{a}\right) + J_1\left(\frac{hQb}{a}\right) + \frac{A}{2}J_2\left(\frac{hQb}{a}\right),$$

and of order $h + 1/Q$ of amplitude

$$\frac{A}{2}J_0\left(\frac{hQb}{a}\right) - J_1\left(\frac{hQb}{a}\right) + \frac{A}{2}J_2\left(\frac{hQb}{a}\right).$$

It is important to bear in mind that Daniel & Lipson, in explaining their experimental observations in terms of a modulation of lattice spacing alone, assumed that the whole of the material in the specimen examined was completely transformed to the modulated structure.

(b) *The physical nature of the modulation*

During the present experimental investigation, the X-ray diffraction data obtained indicated that the transformation of quenched specimens to the modulated structure did not occur simultaneously throughout the specimens, but spread slowly through the specimen. The evidence, and confirmatory microscopic evidence, are given later in §4 (*b*) and (*c*). This observation led to the suggestion that the modulated structure might be the result of a phase change proceeding by the usual process of nucleation and growth, the modulation being produced by a regular arrangement of small volumes of the new phases.

Bradley's data, which show that two tetragonal phases appear after the modulated structure has disappeared, suggest a model for the modulated structure. These tetragonal phases have a common a dimension which is the same as that of the quenched cubic matrix and will therefore fit exactly with each other and the matrix on their basal planes. It is reasonable to assume

* The term 'side-band' is used later to describe the superimposed satellites from many crystals in a powder photograph.

that the nuclei of the tetragonal phases will be coherent with the crystals of the matrix, in which they form, on those planes in which the fit is exact. In directions normal to these planes, the c directions of the tetragonal phases, there is a small degree of misfit, less than 1 %, with the matrix crystal. Bradley also showed that the tetragonal phases were arranged in lamellae whose small dimension was parallel to their c axes. These conclusions have been verified by further experiments during this investigation.

If such lamellae of the two tetragonal phases, Cu-rich and Cu-poor, are arranged alternately and parallel in regular groups then, in a direction parallel to their c axes, the structure exhibits alternate volumes of the Cu-rich and Cu-poor phases, of larger and smaller lattice spacing. This is a very probable arrangement as it minimizes the bulk strains and diffusion distances in the formation of the lamellae from the matrix.

The degree of misfit at the edges of the lamellae is small, and, if the lamellae are thin, it may be that coherence with the matrix is retained on these boundaries, as well as those parallel to the basal planes, as the disregistry introduced by a Cu-rich lamella is opposite in sign to that introduced by a Cu-poor lamella. If coherence is retained on all boundaries, the regular arrangement of lamellae constitutes a periodic modulation of the structure in a direction parallel to the c axis of the tetragonal lamellae. The wave form is approximately rectangular rather than sinusoidal.

(c) *Diffraction by the modulated structure*

The diffraction for such a structure is now calculated in the first instance for one-dimensional models in which the spacing varies, neglecting the variation of scattering factor.

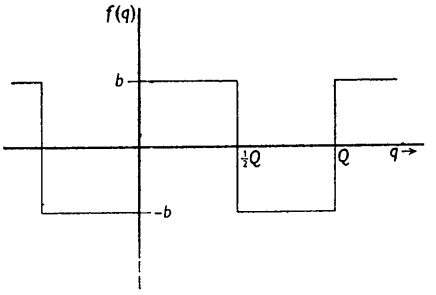


Fig. 2. The variation of lattice parameter as a function of distance parallel to the c axes for lamellae in contact with one another.

The first case considered is that in which the alternate lamellae are in contact with one another and no unchanged matrix remains in the particular group of lamellae considered, although such a group may exist in a specimen in which unchanged cubic matrix occurs elsewhere. The model is illustrated in Fig. 2, in which the variation of lattice parameter, $f(q)$, is plotted against distance measured as a number of unit cells, q, parallel to the c direction. The fundamental assumption is that the lamellae retain coherence with the matrix crystal and merely modulate it, and, therefore, the whole group diffracts coherently. Other minor assumptions are that the wave form is symmetrical, that is, that the lamellae are of equal thickness, and that the departure of the c/a ratio from unity is the same in each case. A Fourier series is used to represent this type of variation, thus:

$$f(q)=\frac{4b}{\pi}\sum_{n=1}^{n=q}\frac{\sin nwq}{n},\quad n \text{ odd},\quad \text{where}\quad w=\frac{2\pi}{Q}.$$

In these calculations l is used rather than h for the order of reflexion, as we have now identified the direction of the modulation with the c axis of the tetragonal phases. The mathematics in detail are to be found elsewhere (Hargreaves, 1949), but the results for the relative amplitudes are:

$$\text{Main reflexion of order } l,\ \text{amplitude}=J_0\left(\frac{4lQb}{\pi a}\right).$$

$$\text{Satellites of order } l\pm p/Q,\ \text{amplitude}=J_p\left(\frac{4lQb}{\pi a}\right).$$

These results are, however, a good approximation only in the range $0<lQb/a<2$. This approximate result is similar to that for a sinusoidal modulation of amplitude $(4/\pi)b$.

For a simultaneous modulation of scattering factor and spacing we may obtain an approximate result by similar methods:

Main reflexion of order l,

$$\text{amplitude}=J_0\left(\frac{4lQb}{\pi a}\right).$$

Satellite of order $l-1/Q$,

$$\text{amplitude}=\frac{2A}{\pi}J_0\left(\frac{4lQb}{\pi a}\right)+J_1\left(\frac{4lQb}{\pi a}\right).$$

Satellite of order $l+1/Q$,

$$\text{amplitude}=\frac{2A}{\pi}J_0\left(\frac{4lQb}{\pi a}\right)-J_1\left(\frac{4lQb}{\pi a}\right).$$

It will become apparent later that the amplitude of the variation of scattering factor is so small that it can be neglected, but it is important to note that in the latter case, in which the simultaneous modulation of scattering power and spacing occurs, the amplitudes of the satellites do not become zero at $l=0$ as they do in the former case in which a modulation of spacing occurs alone.

If the transformation of the single-phase matrix to the tetragonal phases takes place by the usual mechanism of nucleation and growth, there may be a stage, prior to the one represented by the model considered above, in which nuclei or pairs of nuclei occur, separated by volumes of unchanged matrix. The composition and strain relationships make it highly probable that the formation of a nucleus of one tetragonal phase creates in its immediate neighbourhood conditions which lead to the formation of a nucleus of the other conjugate

intermediate phase, and hence the case considered here is that in which pairs of unlike nuclei occur.

The diffraction for a one-dimensional model of such a structure is now considered. In order to simplify the treatment it is assumed that the pairs of nuclei are equally spaced. The model is illustrated in Fig. 3, in which the variation of spacing is plotted against distance in the lattice parallel to the c axes of the nuclei.

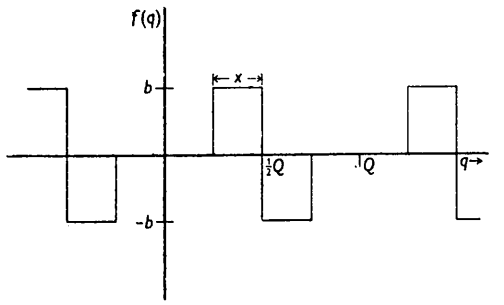


Fig. 3. The variation of lattice parameter as a function of distance parallel to the c axes for pairs of lamellae separated by volumes of unchanged matrix.

Once again a Fourier series is used to represent the variation. The equation for the position of the qth unit of the grating relative to an origin of $q=0$ is written

$$f(q)=qa+\frac{bQ}{\pi}\left[\cos(\delta\pi-1)\cos\frac{2\pi q}{Q}+\frac{1-\cos 2\delta\pi}{4}\cos\frac{4\pi q}{Q}+\frac{\cos 3\delta\pi-1}{9}\cos\frac{6\pi q}{Q}+\ldots\right],$$

where $\delta=2x/Q$, that is, it represents the fraction of the period Q occupied by each pair of nuclei. At $\delta=1$ this expression reverts to the one developed previously for the case in which the lamellae are in contact. The results for the relative amplitudes are:

Main line of order l,

$$\text{amplitude}=J_0\left[\frac{2lQb}{\pi a}(\cos\delta\pi-1)\right]J_0\left[\frac{lQb}{2\pi a}(1-\cos 2\delta\pi)\right].$$

Satellites of order $l\pm 1/Q$,

$$\text{amplitude}=J_0\left[\frac{lQb}{2\pi a}(1-\cos 2\delta\pi)\right]J_1\left[\frac{2lQb}{\pi a}(\cos\delta\pi-1)\right].$$

Satellites of order $l\pm 2/Q$,

$$\text{amplitude}=J_0\left[\frac{2lQb}{\pi a}(\cos\delta\pi-1)\right]J_1\left[\frac{lQb}{2\pi a}(1-\cos 2\delta\pi)\right].$$

The results are approximations for the range $0<lQb/a<2$; their detailed derivation is given elsewhere (Hargreaves, 1949).

The behaviour of these expressions as a function of δ is shown in Fig. 4, which is plotted for $lQb/a=1{\cdot}2$. This is a useful value for later comparison with experimental results, but the actual value does not greatly affect the behaviour. Initially, the satellites at $l\pm 1/Q$ and $l\pm 2/Q$ are of similar amplitude, but as δ increases the satellites at $l\pm 1/Q$, the first-order satellites, become predominant.

It is necessary to extend these results, for the one-dimensional models, to the three-dimensional case, the crystal. A modulation in one direction parallel to the c axis of the tetragonal phases causes satellites to appear at positions corresponding to fractional orders of diffraction $l\pm 1/Q$, etc. In directions parallel to the other two axes the structure exhibits no modulation, as the spacing in these directions is unchanged from that of the cubic matrix, and integral orders only appear. The first-order satellites will therefore occur at positions corresponding to indices of the type $h, k, (l\pm 1/Q)$, where these indices relate to the tetragonal lattice.

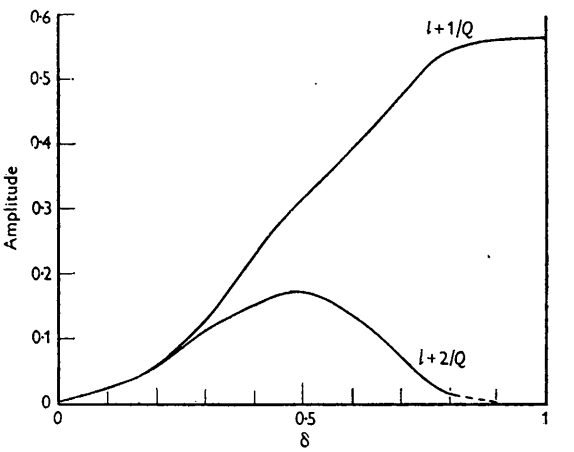


Fig. 4. The amplitudes of the first- and second-order satellites as function of δ for the model represented by Fig. 3 ($\delta=2x/Q$).

In the crystal of the cubic matrix, however, groups of tetragonal lamellae will develop with their c axes parallel to any of the three equivalent cube-axis directions of the matrix; thus each reciprocal-lattice point hkl for the cubic crystal is accompanied, in the modulated structure, by three pairs of first-order satellites—one from each of the three possible orientations of the groups of lamellae—and similarly for satellites of higher orders. As in the cases considered by Daniel & Lipson (see § 2 (*a*) above) the satellites corresponding to a zero value of one of the indices hkl are absent unless a modulation of scattering factor of appreciable amplitude is present.

It is interesting to compare this reciprocal lattice with that corresponding to the original cubic matrix and the lamellae of the two tetragonal phases, without regard to the regular coherent arrangement of lamellae which produces the modulated structure, but assuming only that the tetragonal c axis is always parallel to one of the cube axes. It appears that the groups of satellites in the former reciprocal lattice (i.e. for the (coherent) modulated structure) are replaced by the rod-like shape-transforms of the lamellae in the latter; the satellites are, in fact, maxima within the broad envelope of

reflexion of a tetragonal lamella, arising as a consequence of the regular arrangement of the lamellae.*

The importance of this conclusion becomes obvious in discussing the changes in the diffraction patterns which arise as growth of the lamellae causes loss of coherence with the matrix crystal. For the satellites will be replaced by the broadened reflexions from the independent lamellae, and these broad reflexions will occur over the range of angle of reflexion in which the satellites formerly occurred.

(d) Diffraction patterns for single-crystal and powder specimens

It remains to investigate the nature of the diffraction patterns, first from a single crystal, and secondly from a powder specimen, in which the modulated structure exists.

If the single crystal is orientated with a cube axis as the vertical rotation axis in making rotation patterns, the main reflexions occur at the same positions as those from a quenched single-phase crystal. But whenever the modulated crystal passes through a reflecting position each of the groups of lamellae gives rise to satellites whose separation, from the main reflexion, and intensity are determined by the value of the index of reflexion for the c axes of the particular group. These satellites occur at positions two of whose reciprocal-lattice co-ordinates are identical with those of the associated main reflexion. Thus the satellites occur on the same curve of constant ζ or constant ξ on a Bernal chart, as the main reflexion. The satellites for the two groups of lamellae whose c axes are horizontal therefore occur on the layer line and superimpose if the index for the c axes is the same for each. The satellites from the third group whose c axis is vertical occur above and below the layer line. If one of the indices of the reflecting plane under consideration is zero, one group of lamellae does not give rise to satellites, unless a modulation of scattering factor is present, and thus main reflexions on the zero layer line will not show satellites above and below the layer line, as the index for the vertical axis is zero.

In the powder pattern the main reflexions from many crystals for a particular value of $N=h^2+k^2+l^2$ superimpose to make up the main line and the superimposed satellites are the side-bands. Therefore the ratio of intensity of the sum of the pair of first-order side-bands to the associated main line may be written

$$\frac{I}{I_0}=2\frac{J_1^2\left(\frac{4hQb}{\pi a}\right)+J_1^2\left(\frac{4kQb}{\pi a}\right)+J_1^2\left(\frac{4lQb}{\pi a}\right)}{J_0^2\left(\frac{4hQb}{\pi a}\right)+J_0^2\left(\frac{4kQb}{\pi a}\right)+J_0^2\left(\frac{4lQb}{\pi a}\right)}$$

for a specimen completely transformed to the modulated structure, assuming the variation of scattering factor to be negligible. If a fraction $\mathbf{x}$ of the specimen remains *un*transformed to the modulated structure, that is $b=0$ for this portion, then this fraction makes no contribution to the side-bands, since $J_1(0)=0$, but makes a contribution $3\mathbf{x}$ to the main lines, since $J_0(0)=1$. The expression becomes

$$\frac{I}{I_0}=2\frac{(1-\mathbf{x})\left[J_1^2\left(\frac{4hQb}{\pi a}\right)+J_1^2\left(\frac{4kQb}{\pi a}\right)+J_1^2\left(\frac{4lQb}{\pi a}\right)\right]}{(1-\mathbf{x})\left[J_0^2\left(\frac{4hQb}{\pi a}\right)+J_0^2\left(\frac{4kQb}{\pi a}\right)+J_0^2\left(\frac{4lQb}{\pi a}\right)\right]+3\mathbf{x}}.$$

If more than one non-zero numerical value is present in the indices of the line, then the pattern cannot readily be analysed because the side-bands corresponding to different indices overlap. For the special cases where this is not so, the expression reduces as follows:

For lines of the type (lll),

$$\frac{I}{I_0}=\frac{2J_1^2\left(\frac{4lQb}{\pi a}\right)}{J_0^2\left(\frac{4lQb}{\pi a}\right)+\frac{\mathbf{x}}{1-\mathbf{x}}}.$$

For lines of the type $(ll0)$

$$\frac{I}{I_0}=\frac{4J_1^2\left(\frac{4lQb}{\pi a}\right)}{2J_0^2\left(\frac{4lQb}{\pi a}\right)+1+\frac{3\mathbf{x}}{1-\mathbf{x}}}.$$

For lines of the type $(l00)$

$$\frac{I}{I_0}=\frac{2J_1^2\left(\frac{4lQb}{\pi a}\right)}{J_0^2\left(\frac{4lQb}{\pi a}\right)+2+\frac{3\mathbf{x}}{1-\mathbf{x}}}.$$

To describe the position of the side-bands, use may be made of a modified form of expression developed by Daniel & Lipson from the Bragg equation

$$\frac{Q}{p}=\frac{l\tan\theta}{N.\delta\theta},$$

where $\delta\theta$ is the difference in Bragg angle between the side-band and the main line.

3. Experimental procedure

For a detailed account of the experimental procedure reference may be made to Hargreaves (1949); only a few important points are mentioned below.

The alloy used for most of the work contained 0·7 % residual manganese after deoxidation, but if this impurity is ignored the composition was Cu 49·6, Ni 35·2, Fe 15·2 atomic %, i.e. approximately $Cu_{10}Ni_7Fe_3$. After homogenization of the cast alloy, filings were prepared, annealed under nitrogen to prevent sintering which might result in appreciable X-ray extinction, and quenched sufficiently rapidly to retain the single-phase structure. Small single crystals were

* Cochran (private communication, 1949) has made independent calculations by another method, which are in quantitative agreement with those of the writer; for details, reference may be made to Hargreaves (1949).

isolated from rods subjected to strain-anneal treatments, and specimens for micro-examination were prepared in the usual way.

The powder diagrams were made in a 19 cm. diameter camera of the Bradley–Jay type, using iron $K\alpha_1$ radiation reflected from a curved LiF monochromatizing crystal. The Debye–Scherrer patterns (Fig. 7) showed no $K\alpha_2$ lines and a very low and flat background level. The single-crystal patterns were made in the standard 'Unicam' goniometer.

A Dobson-type photometer was used for the measurement of the powder patterns. The positions of the side-bands were determined from the photometer curves, as eye-estimates of the position of maximum intensity proved very unreliable. The measurement of intensities was rendered more accurate and more reliable as a consequence of relative freedom from the overlapping which occurs when both $K\alpha_1$ and $K\alpha_2$ radiations are present, and the very low and flat background was also very important in securing accuracy, especially for weak diffuse side-bands.

4. Experimental results

Measurements on specimens annealed for periods sufficient to produce the intermediate and equilibrium phases are summarized in Table 1 for the alloy $Cu_{10}Fe_3Ni_7$. As would be expected for the conjugate Cu-rich and Cu-poor phases, the tetragonality of these intermediate phases increases as the temperature of annealing decreases. Also, for the one temperature where the data are complete, the intensity ratios for tetragonal and cubic phases are similar, though it is probably inadvisable to attach much importance to this agreement.

Evidence for the modulated structure was obtained from single-crystal and microscope observations, as well as from powder patterns.

Table 1. *Lattice parameters of intermediate and equilibrium phases for the alloy* $Cu_{10}Ni_7Fe_3$

Intermediate tetragonal phases

Annealing treatment	a (A.)	Cu-rich phase c/a	Cu-poor phase c/a	I_P/I_R*
24 hr., 800° C.	3·586	1·005	0·995	0·79
100 hr., 650° C.	3·586	1·008	0·993	0·77
10 weeks, 550° C.	3·586	1·010	0·991	0·73

Equilibrium cubic phases

Annealing treatment	Cu-rich phase a (A.)	Cu-poor phase a (A.)	I_P/I_R*
10 days, 800° C.	3·594	3·579	0·78

* I_P/I_R is the mean ratio of intensity of the lines of the Cu-poor phase to the corresponding lines of the Cu-rich phase.

(*a*) *Single-crystal patterns*

Complete rotation and 15° oscillation photographs about a cube axis of a matrix crystal, in which the modulated structure had been produced, were made using filtered copper radiation. In Fig. 5 enlargements of individual spots are reproduced, the indices assigned to the spots corresponding to a rotation axis taken to be [001]. The satellites always lay on the same curves of constant ζ or constant ξ as the main reflexions, thus establishing that the modulation takes place along the cube-axis directions of the matrix crystal. Reflexions on the zero layer line exhibited no satellites above and below the layer line, indicating that the variation of scattering factor was negligible. Consideration of the relative intensities of satellites near different reflexions shows that they are in harmony with the model discussed in §2 (*d*) above.

(*b*) *Microscopic observations*

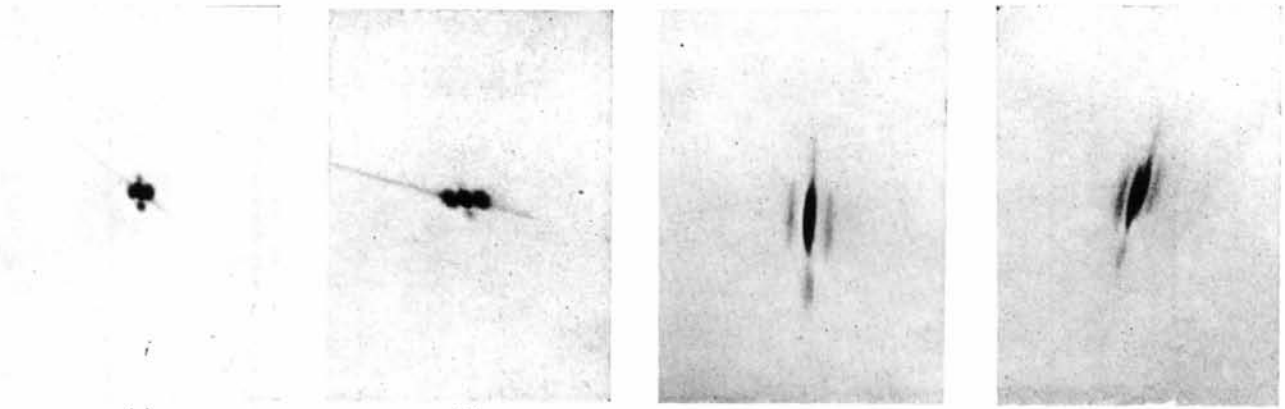
A series of specimens of the alloy $Cu_{10}Ni_7Fe_3$, given various annealing treatments, were examined after mechanical polishing and etching. Photo-micrographs of some of these are shown in Fig. 6. The quenched alloy shows a normal single-phase structure in which annealing twins are present, and the etchant used develops very little grain contrast. After annealing, however, the identical etching treatment darkens some grains very considerably, and, as the duration of annealing increases, more and more grains are affected and the darkening becomes more intense. The darkened grains have a nodular appearance, and this becomes more pronounced after further annealing. No detailed structure can be resolved in the dark nodular grains by means of the optical microscope. After the change of the single-phase alloy to the nodular structure is complete there is a further change to a lamellar structure which may be resolved with difficulty. Further annealing causes an increase in the size of the lamellae until they may be readily resolved.

Comparison with the evidence from the X-ray powder patterns shows that the first darkening which can be observed microscopically corresponds to the first appearance of the modulated structure. The important independent conclusion from the microscopic evidence is that this first change begins at particular points and spreads gradually through the specimen. The later change to the lamellar constituent appears to correspond to the change from the tetragonal intermediate to the cubic equilibrium phases.

(*c*) *Powder diagrams*

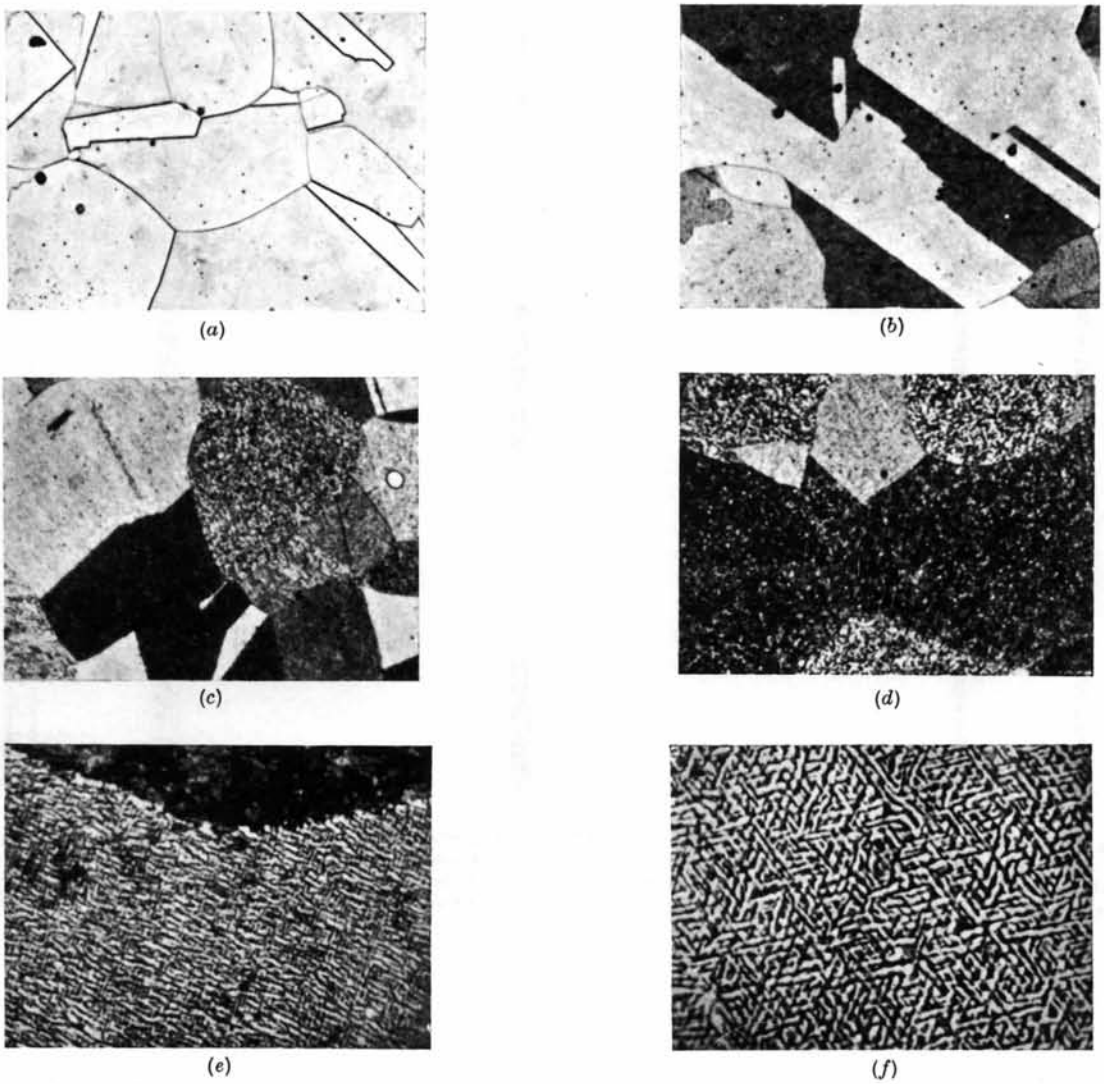
(i) Fig. 7 shows a typical series of patterns for an alloy annealed for increasing periods at a given temperature. The broad diffuse side-bands which appear first move somewhat closer to the main line, become sharper, and in some cases are resolved into first- and second-order side-bands. The side-bands are then replaced by reflexions, at similar positions, characteristic of the presence of two tetragonal phases in the form of independent lamellae.

Table 2 summarizes the results of measurements for a given alloy, after annealing for various times at 550,



(a) (b) (c) (d)

Fig. 5. Enlarged prints of individual reflexions from a single crystal of $Cu_{10}Ni_7Fe_3$ into which the modulated structure had been introduced. Cu $K\alpha$ radiation. (*a*) 111. (*b*) 311 (1st layer line). (*c*) 022 (2nd layer line). (*d*) 222.



(a) (b) (c) (d) (e) (f)

Fig. 6. Photomicrographs of specimens of $Cu_{10}Ni_7Fe_3$ quenched from 1000° C. and annealed for various periods at 800° C. Etchant, saturated solution of potassium dichromate acidified with 1 % concentrated hydrochloric acid and 1 % concentrated sulphuric acid. (*a*) As quenched, × 160. (*b*) Annealed 1 hr., 800° C., × 160. (*c*) Annealed 4 hr., 800° C., × 160. (*d*) Annealed 16 hr., 800° C., × 160. (*e*) Annealed 2 days, 800° C., × 1300. (*f*) Annealed 10 days, 800° C., × 1300.

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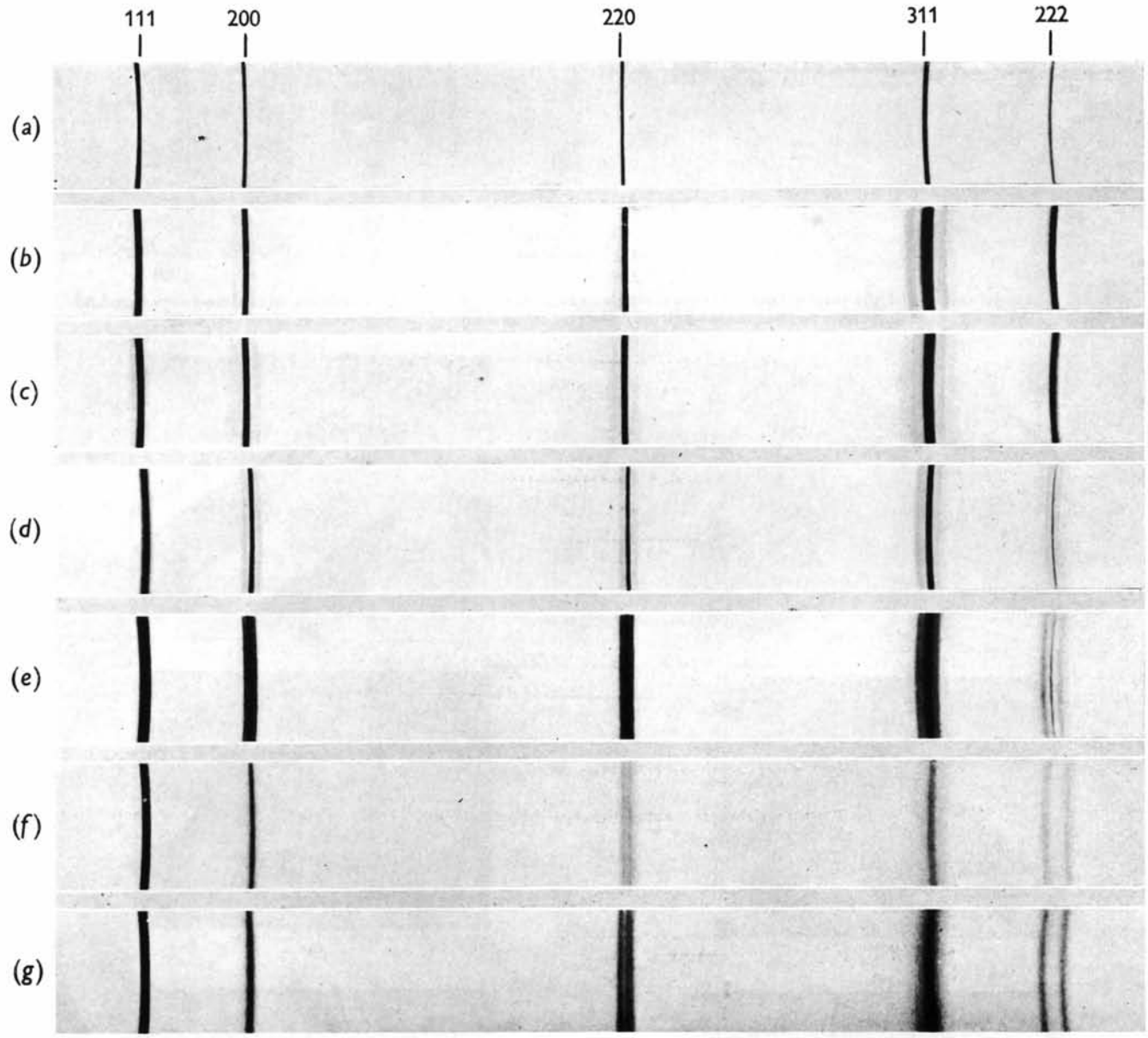

Fig. 7. X-ray diffraction patterns of powder specimens of $Cu_{10}Ni_7Fe_3$ after quenching from 950° C. and annealing for various periods at 550° C. Fe $K\alpha_1$ radiation. (*a*) As quenched, single phase f.c.c. (*b*) Annealed 3 hr., 550° C., modulated structure. (*c*) Annealed 8 hr., 550° C., modulated structure. (*d*) Annealed 56 hr., 550° C., modulated structure. (*e*) Annealed 6 days, 550° C., modulated structure. (*f*) Annealed 3 weeks, 550° C., two tetragonal phases. (*g*) Annealed 10 weeks, 550° C., two tetragonal phases.

650 and 800° C. The wave-length, Q, of the modulation is calculated from the measured separation of the side-bands, using the expression given in § 2 (*d*). The amplitude b/a (i.e. $|(c-a)/a|$) is obtained from the parameters of the tetragonal phases which separate at the various temperatures (Table 1). In a given pattern, the values of Q derived from the different lines agree within the limits of error of measurement. It is found that Q remains fairly constant for a considerable range of time of annealing prior to the change to the tetragonal pattern. Also, $Qb/2a$—the total disregistry, at the edges of the tetragonal lamellae, over one-half wave-length (i.e. over one lamella)—is nearly constant for the various temperatures; it is reasonable to suppose that this represents a limiting misfit for coherence of the modulated structure, and that more prolonged annealing results in the production of independent tetragonal lamellae. This limiting value of the thickness to which the coherent lamellae may grow may be a factor, operating during the formation of the structure, which is responsible for the regularity of thickness of the lamellae which produce the modulated structure (see also § 4 (*d*) below).

Table 2. *Wave-lengths (Q) of the modulated structures produced by various annealing treatments of the alloy* $Cu_{10}Ni_7Fe_3$

56 hr., 550° C.		6 days, 550° C.		
Line	Q from 1st order	Line	Q from 1st order	Q from 2nd order
111	70	111	62	—
200	63	200	72	69
220	69	220	69	—
311	65	311	69	70
222	64	222	65	—
Mean	65	Mean	67	Mean $Qb/a=0{\cdot}66$
1 hr., 650° C.		4 hr., 650° C.		
Line	Q from 1st order	Line	Q from 1st order	Q from 2nd order
111	67	111	75	—
200	72	200	70	—
220	68	220	70	—
311	72	311	74	71
222	70	222	74	—
Mean	70	Mean	73	Mean $Qb/a=0{\cdot}60$
½ hr., 800° C.		1 hr., 800° C.		
Line	Q from 1st order	Line	Q from 1st order	Q from 2nd order
111	—	111	—	—
200	118	200	127	—
220	136	220	120	—
311	139	311	139	136
222	120	222	144	—
Mean	126	Mean	132	Mean $Qb/a=0{\cdot}67$

(ii) In the initial stages of annealing, broad side-bands are seen, which (on photometry) show no definite positions of maximum intensity, and are too weak to permit measurement of their intensity relative to the main line. A satisfactory qualitative interpretation is that small pairs of lamellae, somewhat irregularly distributed, and separated by volumes of unchanged matrix, are giving rise to overlapping side-bands of first and second orders, of similar intensities. The slight increase in average wave-length between this and later patterns may be due to some like lamellae growing into contact as the transformation proceeds.

(iii) Formulae developed in § 2 (*d*) relate the intensity of the side-bands to that of the main line, for lines with various indices (*hkl*). In comparing these relations with experimental measurements, a difficulty arises because **x**, the fraction of the specimen remaining *un*transformed, cannot be determined.* The procedure adopted is to use the measurements for one line in a pattern (the line (222) in Table 3) to determine **x** for that specimen and treatment, and to use this value of **x** to compare observed and calculated values of I/I_0 for the other lines of that pattern. The agreement obtained in this way is satisfactory, and confirms that the model proposed for the modulated structure is essentially correct. The increase of intensity of the side-bands (at almost constant wave-length) prior to the disappearance of the modulated structure is thus explained as due to the increase in the fraction of the specimen transformed.

Table 3. *Comparison of calculated and observed intensities of side-bands for specimens receiving various treatments*

Specimen and **x** (calc.)	Line	I/I_0 calc.	I/I_0 obs.
56 hr., 550° C. **x**=0·38	222	0·84	0·84*
	220	0·42	0·45
	200	0·17	0·22
6 days, 550° C. **x**=0·02	222	3·72	3·72*
	220	0·98	1·10
	200	0·30	0·33
	111	0·44	0·35
1 hr., 650° C. **x**=0·30	222	0·99	0·99*
	220	0·47	0·52
	200	0·18	0·24
	111	0·14	0·16
4 hr., 650° C. **x**=0·17	222	1·31	1·31*
	220	0·58	0·59
	200	0·21	0·23
	111	0·24	0·19
½ hr., 800° C. **x**=0·32	222	1·06	1·06*
	220	0·49	0·44
	200	0·19	0·22
1 hr., 800° C. **x**=0·11	222	2·26	2·26*
	220	0·79	0·81
	200	0·26	0·23

* The values for this line are used to calculate **x**, the fraction *un*transformed; observed and calculated values, therefore, always agree.

(iv) Attempts to obtain quantitative experimental evidence for the enhancement of side-bands of higher order, predicted by the theory for main lines of high order, were unsuccessful. Using iron $K\alpha_1$ radiation only the lines up to $N=12$ are recorded; with copper

* Microscopic examination of a solid specimen cannot be assumed to give a measure of the rate of transformation in a powder.

$K\alpha_1$ radiation, which gives lines up to $N=20$, the fluorescent radiation gives a background so heavy as to make accurate photometric measurement impossible, and it is possible to say only that approximate estimates of intensity are in harmony with theoretical predictions.

(v) In (iii) above (and in Table 3), the *mean* side-band intensity is compared with the intensity of the main line. The two side-bands of a pair are, however, asymmetric, and it was found that the intensity ratio I_H/I_L lay in the range 0·67–0·80 (where I_H refers to the high-angle side-band of order $l+1/Q$, I_L to the low-angle side-band of order $l-1/Q$). That this asymmetry is not due to a modulation of the scattering power is shown both by the single-crystal patterns (§ 4 (*a*) above) and by calculation from the known compositions of the equilibrium phases.

The values of I_P/I_R in Table 1 lie in the same range of values as I_H/I_L for the side-bands, and it is reasonable to suppose that the asymmetry is due to a difference in the amounts of the two phases present. This was confirmed by experiments with alloys Cu_6Ni_3Fe and Cu_3Ni_3Fe, for which I_P/I_R is appreciably different from unity; the early stages of annealing are similar to those for the modulated structure in $Cu_{10}Ni_7Fe_3$, but further annealing next causes the appearance of one cubic equilibrium phase and one tetragonal intermediate phase, before the final conversion to two cubic phases. Table 4 contains the results of measurements on the alloys in the second and third stages; the values of I_H/I_L, determined approximately for the first stage, were similar to the values of I_P/I_R, thus confirming the relation between the asymmetry of the side-bands and the proportion of the two phases separating.

Table 4. *Parameters in Ångström units of phases separating during annealing in the alloys* Cu_6FeNi_3 *and* Cu_3FeNi_3

	First stage, 8 hr., 650° C.		
Alloy	Cu-rich phase	Cu-poor phase	I_P/I_R
Cu_6FeNi_3, quenched, $a=3{\cdot}584$ A.	Cubic $a=3{\cdot}592$ A.	Tetragonal $a=3{\cdot}584$ A. $c/a=0{\cdot}990$	0·5
Cu_3FeNi_3, quenched, $a=3{\cdot}577$ A.	Tetragonal $a=3{\cdot}577$ A. $c/a=1{\cdot}006$	Cubic $a=3{\cdot}567$ A.	1·4
	Second stage, 100 hr., 650° C.		
Alloy	Cu-rich phase	Cu-poor phase	I_P/I_R
Cu_6FeNi_3, quenched, $a=3{\cdot}584$ A.	Cubic $a=3{\cdot}592$ A.	Cubic $a=3{\cdot}568$ A.	0·5
Cu_3FeNi_3, quenched, $a=3{\cdot}577$ A.	Cubic $a=3{\cdot}590$ A.	Cubic $a=3{\cdot}567$ A.	1·4

(*d*) *Magnetic and mechanical properties*

A preliminary investigation of the magnetic and mechanical properties of the alloy $Cu_{10}Ni_7Fe_3$ has been carried out in this laboratory in association with Prof. W. Sucksmith at Sheffield University (Arndt, 1948). The results indicate that the mechanical hardness, remanence and coercivity of the quenched alloys increase as annealing proceeds, reach a maximum and then decrease. The data available do not allow the positions of the maxima, for various temperatures, in the scale of time of annealing to be fixed accurately, but it appears that the positions of the maxima, for mechanical hardness and remanence at least, lie in the range of annealing in which the limit of existence of the modulated structure has been found to occur in the present investigation. It has been suggested here that the disappearance of the modulated structure corresponds to the loss of coherence of the lamellae of the tetragonal phases at their edges, where coherency strains due to disregistry arise. This view is supported by these observations of magnetic and mechanical properties as the building up and eventual release of coherency strains would account for the maxima observed in these properties.

5. Discussion

In this investigation it has been shown that X-ray diffraction effects observed for the Cu–Ni–Fe alloys studied can be accounted for qualitatively by considering the structure to be made up of a regular arrangement of lamellae of the tetragonal intermediate phases, which form on annealing but retain their coherence with the cubic matrix crystal and modulate it. Subsequently the tetragonal phases lose coherence with the matrix crystal and later transform to the cubic equilibrium phases. Within the limits imposed by the photographic technique employed, satisfactory quantitative agreement between theory and experiment is obtained. The modulation of the matrix crystal takes place in the directions of the cube axes and is predominantly one of lattice parameter.

This interpretation is essentially similar to that of Daniel & Lipson, differing from it in the assumption of a rectangular wave form for the modulation, and in the emphasis placed on the idea that the transformation proceeds by nucleation and growth; the physical picture of the process is much more easily visualized than is that previously proposed.

The limit of existence of the modulated structure occurs when the disregistry at the edge of the lamellae reaches a total value of approximately one-third of a cell edge, and the previously completely coherent lamellae then lose coherence on all but the basal planes. Further annealing causes loss of coherence even on these planes, as the tetragonal phases transform to cubic phases of spacings differing from one another.

Geisler & Newkirk (1949) have investigated the Cu–Ni–Co permanent-magnet alloys, which behave very similarly to the Cu–Ni–Fe alloys in the later stages of annealing. It appears, however, that quenching is not sufficient to retain the single-phase state, the corresponding X-ray pattern being similar to that for Cu–Ni–Fe at the stage when the modulated structure is

changing to that of two tetragonal phases. The explanation advanced by Geisler & Newkirk is somewhat more complicated, and requires *ad hoc* assumptions which appear to the present writer to be unnecessary.

In discussing the experimental observations, care has been taken to emphasize that in the modulated structure the small regions of tetragonal material preserve coherence with the matrix. In §2(*c*), however, the relationship of this structure to that containing *small* independent 'particles' of the two tetragonal phases has been considered. In particular, it has been shown that the satellites in the diffraction pattern from the modulated lattice lie within the broad envelopes of reflexion which would arise from small independent particles. These considerations suggest that in the case of alloys of the age-hardening type examined by Guinier, Preston and others, and more recently by Geisler & Hill (1948), the difference in the interpretations proposed for the diffraction patterns may be more apparent than real.

A further point of interest which emerges from the work described above is the observation that the transformation can be detected microscopically when the X-ray pattern is that of the modulated structure, long before the pattern changes to that characteristic of the intermediate phases.

The Cu–Ni–Fe alloys show the properties of permanent magnets, as do the Cu–Ni–Co alloys, and the modulated structure appears in both cases. Permanent-magnet alloys of the 'Alcomax' group have been investigated by Oliver & Goldschmidt (1946), and some evidence of the existence of a modulated structure in this group has been found. The limited evidence so far available indicates that the magnetic properties of the Cu–Ni–Fe alloys are affected systematically by the development of the modulated structure. It seems that the property of permanent magnetism may be intimately connected with the modulated structure in these and perhaps in other systems.

I wish to thank Prof. Sir Lawrence Bragg for valuable discussions during the course of the investigation, and Dr W. H. Taylor for his helpful suggestions and interest throughout. Thanks are also due to Mr A. D. I. Nicol, who introduced the writer to the problem and collaborated in early experiments on the use of monochromators.

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