

## Correlative Microdomain Model for Short-Range Ordered Alloy Structures. I. Diffraction Theory

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A diffraction theory is developed for diffuse scattering from disordered binary alloys with short-range order. It is based on a model of ordered microdomains embedded in a disordered matrix and interference effects between the domains are considered. There is a possibility that the fine structures of diffuse scattering as observed in the cases of  $\text{Cu}_3\text{Au}$ ,  $\text{CuAu}$  and  $\text{Cu}_3\text{Pd}$  alloys result from the introduction of interdomain correlations. From experimental diffuse intensity values one can calculate the statistical distribution of microdomains in antiphase with one another.

### Introduction

In order to describe atomic configuration of disordered binary alloys with short-range order (SRO), the Warren parameters ( $\alpha_i$ 's), which give exact correlations between the two kinds of atoms, are generally used (Cowley, 1950). They are defined by

$$\alpha_i = 1 - p_i^{\text{AB}}/m_{\text{B}} \quad (\text{or} = 1 - p_i^{\text{BA}}/m_{\text{A}}),$$

where  $p_i^{\text{AB}}$  is the probability of finding a B atom at the extremity of the vector  $\mathbf{R}_i$  with its origin at an A atom, and  $p_i^{\text{BA}}$  is defined in a similar way;  $m_{\text{A}}$  and  $m_{\text{B}}$  are the fractions of A and B atoms in the alloy. A set of SRO parameters can be uniquely obtained from the Fourier transformation of diffuse scattering and this has been considered as very important and convenient for treating the problems of binary alloys in diffraction theory as well as in statistical theory.

However, correlation functions such as a set of  $\alpha_i$  parameters do not offer, by themselves, any further information as to the real atomic arrangements in an alloy. Therefore, some physical aspects must be considered if it is required to find the microstructures or the local atomic arrangements in disordered alloys with SRO. Up to the present, various attempts to find such atomic configurations have been made by diffractionists using various assumptions. For the  $\text{Cu}_3\text{Au}$  alloy, Batterman (1956) and Moss (1966) proposed a model similar to Wilson's (1962) treatment, in which a disordered state is approached by introducing 'bad' mistakes (or high-energy antiphase boundaries) in addition to 'good' mistakes (or low-energy antiphase boundaries). Recently, a model was proposed by Greenholz & Kidron (1970) which represented a structure of microdomains embedded *randomly* in a disordered matrix. A computer simulation by Gehlen & Cohen (1965) supported the existence of minute ordered domains in a nearly random matrix. This structure may be considered as a geometrically possible one when the  $\alpha_i$  parameters in the region of small interatomic distance are given.

An electron diffraction pattern from the  $\text{Cu}_3\text{Au}$  alloy was obtained by Hashimoto & Ogawa (1970) in which the diffuse scattering was characterized by four diffuse streaks running along the  $\langle 110 \rangle$  directions as shown in Fig. 1(a) and schematically illustrated in Fig. 1(b). The pattern is considered to be the most highly resolved which has ever been observed from the disordered  $\text{Cu}_3\text{Au}$  alloy. In the disordered  $\text{Cu}_3\text{Pd}$ , a diffraction pattern similar to that from  $\text{Cu}_3\text{Au}$  was observed by Watanabe (1959), and recently by Oshima & Watanabe (1973), as shown in Fig. 2. No structure analysis has been done for diffuse scattering with this type of fine structure.

In the present paper, a diffraction theory is developed for such SRO binary alloys, based on a model of ordered microdomains embedded in a perfectly disordered matrix, as schematically illustrated in Fig. 3. The fine structure of diffuse scattering around the superlattice-reflexion positions is obtained by the introduction into the model of *correlations* between microdomains out of phase with one another. This model may well embody the microstructure of disordered alloys with SRO. The model of Greenholz & Kidron (1970) neglects the interference effect between minute ordered regions and therefore cannot explain the fine structure of diffuse scattering. Watanabe (1959) suggested that in  $\text{Cu}_3\text{Pd}$ , which has a long-period structure below the order-disorder transition temperature, short chains of one-dimensional antiphase domains with the same period of step shifts as in the ordered state may remain randomly in a disordered state. Moss (1966) also mentioned that it was reasonable to assume a very high density of small highly ordered regions in antiphase to one another existing in a nearly random matrix for the disordered  $\text{Cu}_3\text{Au}$  alloy. The present theory treats such a minute antiphase domain model more strictly and quantitatively. Further, the present model, which will be called the correlative microdomain model (CMDM), is shown to be plausible in the following brief consideration. According to Moss (1969), the streaks lie at the distance

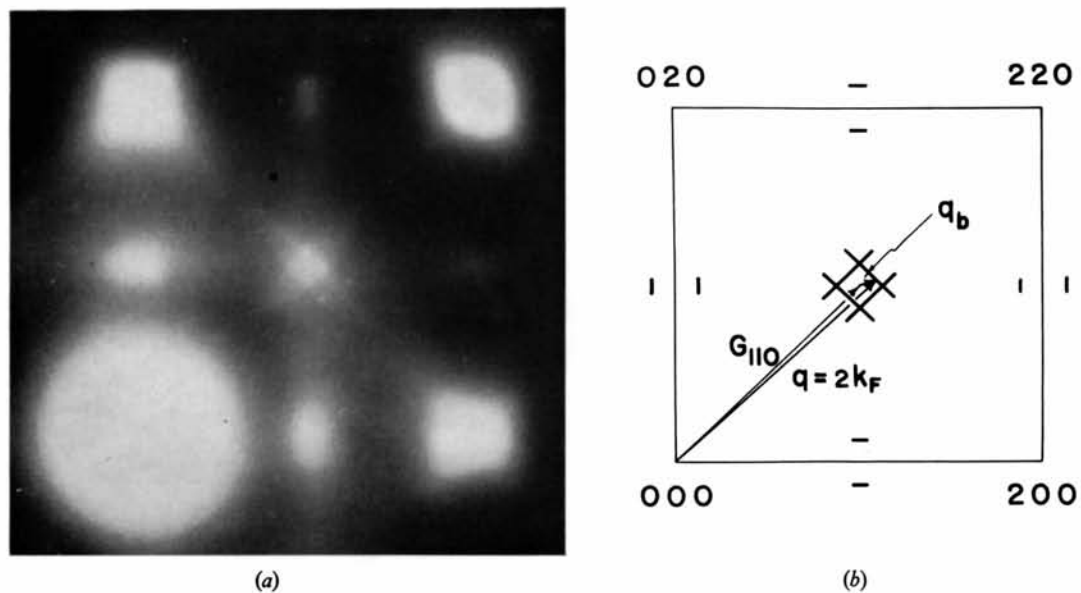


Fig 1. (a) Diffraction pattern taken from  $\text{Cu}_3\text{Au}$  quenched from  $450^\circ\text{C}$ . (b) Illustration of (a).  $G_{110}$  is the superlattice reflexion position of the  $L_2$   $\text{Cu}_3\text{Au}$  ordered structure.  $q$  shows the position of strong diffuse intensity.  $q_b = q - G_{110}$ .

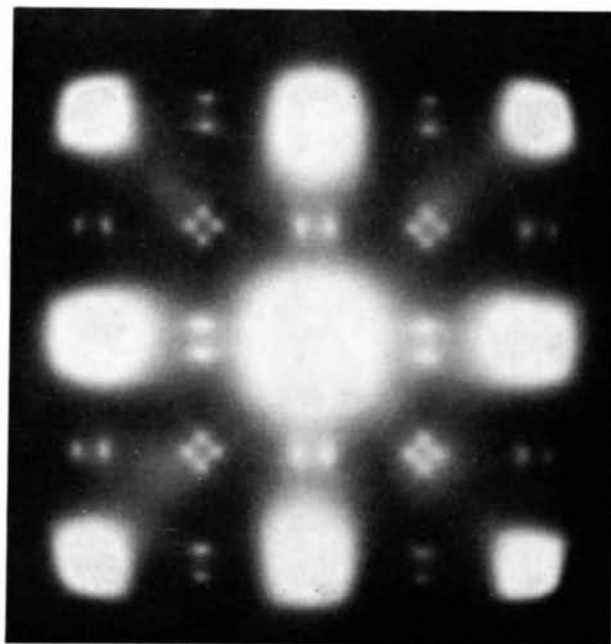


Fig. 2. Diffraction pattern taken from  $\text{Cu}_3\text{Pd}$  quenched from  $500^\circ\text{C}$ . (From Oshima & Watanabe, 1973).

$\mathbf{q} = 2\mathbf{k}_F$  ( $\mathbf{k}_F$  is the Fermi wave vector on the flat part of the Fermi surface) from the fundamental reciprocal-lattice points, and the existence of them means that the Fermi surface produces a relatively long-range oscillatory interatomic interaction with the wave vector  $\mathbf{q} = 2\mathbf{k}_F$  in real space. In the  $\text{Cu}_3\text{Au}$  alloy, the vector  $\mathbf{q} = 2\mathbf{k}_F$  lies close to the superlattice position  $\mathbf{G}_{110}$ , and, therefore, the oscillation agrees approximately with the periodicity of the  $L1_2$  ordered structure and stabilizes this structure within minute regions in the disordered state. A wave, whose wave vector is the difference  $\mathbf{q}_b$  [shown in Fig. 1(b)] between  $\mathbf{q} = 2\mathbf{k}_F$  and  $\mathbf{G}_{110}$  as shown in the lowest part of Fig. 4, is considered to bring an antiphase relation to any pair of microdomains with a definite interval.

### Theory of diffraction

The amplitude diffracted from a binary alloy crystal can be written as

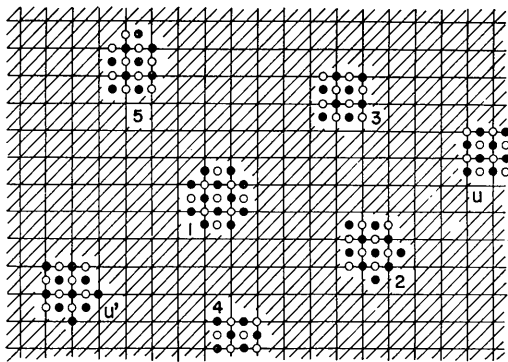


Fig. 3. Microdomain structure of antiphase domains embedded in a disordered matrix with any correlation between them. The shaded region indicates the disordered region.

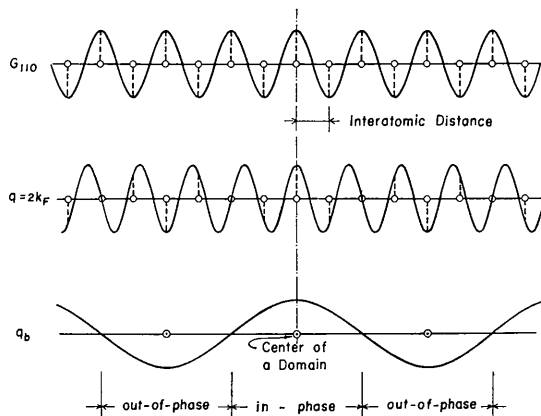


Fig. 4. Schematic illustration of the waves with wave vectors  $\mathbf{G}_{110}$ ,  $\mathbf{q} = 2\mathbf{k}_F$  and  $\mathbf{q}_b$ , respectively, which are projected on one direction.

$$A(\mathbf{q}) = \sum_i \{f^i + f(\mathbf{R}_i)\} \exp(-2\pi i \mathbf{q} \cdot \mathbf{R}_i), \quad (1)$$

$$f^i = m_A f_A + m_B f_B,$$

where  $f_A$  and  $f_B$  are the atomic scattering factors of A and B atoms, respectively, and  $f(\mathbf{R}_i)$  represents a deviation of the atomic scattering factor of an atom on an  $i$  site from  $f^i$ , the average scattering factor, and equals  $+m_B(f_A - f_B)$  or  $-m_A(f_A - f_B)$  according to whether the  $i$  site is occupied by an A atom or a B atom.  $\mathbf{q}$  is the scattering vector whose modulus is  $2(\sin \theta)/\lambda$ ,  $2\theta$  being the scattering angle and  $\lambda$  the wavelength.  $\mathbf{R}_i$  is a vector from the origin to the  $i$  site.

The intensity of the diffracted beam is written as

$$I(\mathbf{q}) = A(\mathbf{q})A^*(\mathbf{q})$$

$$= |f^i|^2 \sum_i \sum_j \exp[-2\pi i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)]$$

$$+ \sum_i \sum_j \{f(\mathbf{R}_i)f^{i*} + f^{j*}f(\mathbf{R}_j)\} \exp[-2\pi i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)]$$

$$+ \sum_i \sum_j f(\mathbf{R}_i)f^*(\mathbf{R}_j) \exp[-2\pi i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)]. \quad (2)$$

In equation (2) the first term gives the fundamental reflexions, and the second term is equal to zero because  $\sum_i f(\mathbf{R}_i) = \{m_A(+m_B) + m_B(-m_A)\}(f_A - f_B) = 0$ . The third term is the diffuse scattering due to SRO, and will appear throughout the present treatment.

It is assumed that ordered microdomains are embedded in a disordered matrix without any SRO. In this case the third term in equation (2), denoted by  $I_{\text{sro}}(\mathbf{q})$ , can be expressed as

$$I_{\text{sro}}(\mathbf{q}) = \sum_r \sum_{r'} f(\mathbf{R}_r)f^*(\mathbf{R}_{r'}) \exp[-2\pi i \mathbf{q} \cdot (\mathbf{R}_r - \mathbf{R}_{r'})]$$

$$+ \sum_r \sum_j f(\mathbf{R}_r)f^*(\mathbf{R}_j) \exp[-2\pi i \mathbf{q} \cdot (\mathbf{R}_r - \mathbf{R}_j)]$$

$$+ \sum_i \sum_{r'} f(\mathbf{R}_i)f^*(\mathbf{R}_{r'}) \exp[-2\pi i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_{r'})]$$

$$+ \sum_i \sum_j f(\mathbf{R}_i)f^*(\mathbf{R}_j) \exp[-2\pi i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)], \quad (3)$$

where the subscripts  $r$  and  $r'$  denote the sites in the disordered matrix, and  $i$  and  $j$  the sites in the ordered microdomains. The first term in equation (3) becomes the Laue monotonic scattering that results only from the disordered volume of the crystal and is indicated as  $I_{\text{LM}}$ . That is to say,

$$I_{\text{LM}} = n_r m_A m_B |f_A - f_B|^2, \quad (4)$$

where  $n_r$  is the number of atoms in the disordered volume. Only the terms for  $r = r'$  remain in the double sum of the first term. The second and third terms in equation (3) vanish, because there is no correlation between  $f(\mathbf{R}_r)$  and  $f(\mathbf{R}_j)$ , or  $f(\mathbf{R}_i)$  and  $f(\mathbf{R}_{r'})$ . The last term expresses the diffraction effect from ordered microdomains on the diffuse scattering, and can be rewritten as

$$I_{\text{MD}}(\mathbf{q}) = \sum_i \sum_j f'(\mathbf{R}_i)f'^*(\mathbf{R}_j)$$

$$\times \exp[-2\pi i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)], \quad (5)$$

where the summations are over the whole crystal volume and  $f'(\mathbf{R}_i)$  and  $f'(\mathbf{R}_j)$  are defined as

$$f'(\mathbf{R}_i) \text{ [or } f'(\mathbf{R}_j)] = \begin{cases} f(\mathbf{R}_i) \text{ [or } f(\mathbf{R}_j)] & \text{in the ordered microdomains} \\ 0 & \text{in the disordered matrix.} \end{cases}$$

By using the factors  $f(\mathbf{R}_i)$ 's in this way, we may formally divide the diffuse scattering equation into the two terms, equations (4) and (5), from the ordered and disordered volumes.

The aspect of a microdomain structure is schematically illustrated in Fig. 3. Microdomains labelled as 1, 4 and  $u$  are in phase with one another while the others are also in phase with one another, but, the former group, which is called the 1st type of order, is out of phase with the latter group which is called the 2nd type of order. An example of the distinction of the order types is given in Appendix I.

The shape function  $E_u(\mathbf{R}_i)$  is defined here as follows;

$$E_u(\mathbf{R}_i) = \begin{cases} 1 & \text{inside the domain labelled as } u \\ 0 & \text{outside the domain } u. \end{cases} \quad (6)$$

$f'(\mathbf{R}_i)$  is written in terms of the shape function  $E_u(\mathbf{R}_i)$ , *i.e.*

$$f'(\mathbf{R}_i) = \sum_u f_u(\mathbf{R}_i) E_u(\mathbf{R}_i). \quad (7)$$

$f_u(\mathbf{R}_i)$ 's are the factors defined in the whole regular atomic lattice as taking the values of the  $f(\mathbf{R}_i)$ 's for the perfectly ordered structure in phase with the domain  $u$ . The subscript  $u$  of  $f_u(\mathbf{R}_i)$  and  $E_u(\mathbf{R}_i)$  indicates both the label of the domain and the type of ordered structure. The intensity equation (5) for the diffuse scattering is rewritten as

$$I_{\text{MD}}(\mathbf{q}) = \sum_i \sum_j \sum_u \sum_{u'} f_u(\mathbf{R}_i) f_{u'}^*(\mathbf{R}_j) E_u(\mathbf{R}_i) E_{u'}(\mathbf{R}_j) \times \exp[-2\pi i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)]. \quad (8)$$

We will use an average shape function  $E_t(\mathbf{r})$  having a centre at  $\mathbf{r}=0$  where  $\mathbf{r}$  represents a vector in real space, instead of the shape function  $E_u(\mathbf{R}_i)$  corresponding to the individual domains, if the domains belong to the same  $t$ th type of ordered structure, *i.e.* they are in phase with one another.  $\mathbf{X}_u$  is defined here as a centre of the function  $E_t(\mathbf{r}_u)$  corresponding to a domain  $u$ , where  $\mathbf{r}_u = \mathbf{R}_i - \mathbf{X}_u$  indicates a vector of an atomic site with respect to  $\mathbf{X}_u$ . The average function  $E_t(\mathbf{r})$  is discussed in detail in Appendix II. Equation (8) can be rewritten by using the average function  $E_t(\mathbf{r})$  and the relation  $\mathbf{R}_j = \mathbf{R}_i + \mathbf{R}_l$  and  $\mathbf{X}_{u'} = \mathbf{X}_u + \mathbf{X}_{uu'}$  as follows:

$$I_{\text{MD}}(\mathbf{q}) = m_A m_B |f_A - f_B|^2 \sum_t \sum_{u'} C_t^{(tt')} \exp(2\pi i \mathbf{q} \cdot \mathbf{R}_l) \times \sum_i E_t(\mathbf{R}_i - \mathbf{X}_u) E_{t'}(\mathbf{R}_i - \mathbf{X}_u + \mathbf{R}_l - \mathbf{X}_{uu'}), \quad (9)$$

where

$$C_t^{(tt')} = \frac{1}{m_A m_B |f_A - f_B|^2} f_t(\mathbf{R}_i) f_{t'}^*(\mathbf{R}_i + \mathbf{R}_l), \quad (10)$$

and the subscripts  $t$  and  $t'$  indicate the types of order of microdomains  $u$  and  $u'$ , respectively, and  $f_t(\mathbf{R}_i)$  in equation (10) the  $f(\mathbf{R}_i)$  value for the perfectly ordered structure of the  $t$ th type. In equation (9), the product  $f_u f_{u'}^*$  from equation (8) is closely approximated by an average, which is carried out over pairs of atomic sites separated by the vector  $\mathbf{R}_l$ , as expressed in equation (10). The factor  $C_t^{(tt')}$  is like the  $\alpha_t$  parameter for a perfectly ordered structure, but since the atoms of the pair refer to the different types of order  $t$  and  $t'$  respectively, the factor can be regarded as a kind of phase factor between the  $t$  and  $t'$ th types of order.

Let  $P_{t'}(\mathbf{X})d\mathbf{X}$  be the probability of finding the centre of another ordered microdomain with the  $t'$ th type of order in the volume  $d\mathbf{X}$  at the extremity of the vector  $\mathbf{X}$ , whose origin is at the centre of a microdomain of the  $t$ th type of order. The value of  $P_{t'}(\mathbf{X})$  fluctuates about the mean density of microdomains of the  $t'$ th order type when  $|\mathbf{X}|$  is small, and tends toward the mean density when  $|\mathbf{X}|$  assumes a large value.  $P_{t'}(\mathbf{X})$  corresponds to the distribution  $P(\mathbf{x})$  of the atoms at the extremity of the vector  $\mathbf{x}$  whose origin is at an atom and was described in detail by Guinier (1963). Thus, equation (9) can be written as

$$I_{\text{MD}}(\mathbf{q}) = I_{\text{MD}}^0(\mathbf{q}) + I_{\text{MD}}^i(\mathbf{q}), \quad (11a)$$

$$I_{\text{MD}}^0(\mathbf{q}) = \frac{m_A m_B}{v_0} |f_A - f_B|^2 \sum_t \sum_{t'} N_t C_t^{(tt')} \times \int E_t(\mathbf{r}) E_{t'}(\mathbf{r} + \mathbf{R}_l) d\mathbf{r} \exp(2\pi i \mathbf{q} \cdot \mathbf{R}_l), \quad (11b)$$

$$I_{\text{MD}}^i(\mathbf{q}) = \frac{m_A m_B}{v_0} |f_A - f_B|^2 \sum_t \sum_{t'} \sum_{t''} N_t C_t^{(tt'')} \int \int P_{t''}(\mathbf{X}) \times E_t(\mathbf{r}) E_{t'}(\mathbf{r} + \mathbf{R}_l - \mathbf{X}) d\mathbf{r} d\mathbf{X} \exp(2\pi i \mathbf{q} \cdot \mathbf{R}_l), \quad (11c)$$

where the sums over  $t$  and  $t'$  are taken for all the possible types of order, and  $N_t$  is the number of microdomains of the  $t$ th type of order. The sum over  $i$  is replaced by an integral form  $(1/v_0) \int \dots d\mathbf{r}$ , where  $v_0$  is the volume of the crystal per atom, taking into consideration that the centres of the microdomains  $\mathbf{X}_u$  are not necessarily situated on the periodic lattice points and the vectors  $(\mathbf{R}_i - \mathbf{X}_u)$  exist continuously over the whole of real space.  $I_{\text{MD}}^0(\mathbf{q})$  is the intensity which would be obtained if there were no correlations between microdomains, and it gives the diffuse scattering around the superlattice reflexion points which are broadened by the size effect of ordered microdomains.  $C_t^{(tt')}$  corresponds to the  $\alpha_t$  parameter in a perfectly ordered alloy of the  $t$ th type.  $I_{\text{MD}}^i(\mathbf{q})$  expresses an interference term due to the correlations between microdomains.

Equations (11a, b and c) are written in a more useful form by introducing the Fourier transforms of  $C_t^{(tt')}$  and  $E_t(\mathbf{r})$ , *i.e.*

$$C_i^{(tr)} = \sum_{\mathbf{G}}^{(\text{BZ})} \gamma_{\mathbf{G}}^{(tr)} \exp(-2\pi i \mathbf{G} \cdot \mathbf{R}_i), \quad (12)$$

$$E_i(\mathbf{r}) = \int \varepsilon_i(\mathbf{q}') \exp(2\pi i \mathbf{q}' \cdot \mathbf{r}) d\mathbf{q}'. \quad (13)$$

In equation (12) the sum is over all the reciprocal-lattice points (both the fundamental-lattice and superlattice points for the ordered structures) in the first Brillouin zone for the disordered lattice. Inserting equations (12) and (13) into equations (11b and c), we obtain

$$I_{\text{MD}}^0(\mathbf{q}) = \frac{m_A m_B}{v_0^2} |f_A - f_B|^2 \sum_{\mathbf{G}_i} \sum_{\mathbf{r}} N_i \gamma_{\mathbf{G}_i}^{(tt)} \varepsilon_i^2(\mathbf{q} - \mathbf{G}_i), \quad (14a)$$

$$I_{\text{MD}}^i(\mathbf{q}) = \frac{m_A m_B}{v_0^2} |f_A - f_B|^2 \sum_{\mathbf{G}_i} \sum_{\mathbf{r}} \sum_{\mathbf{r}'} N_i \gamma_{\mathbf{G}_i}^{(tr')} \times \varepsilon_i(\mathbf{q} - \mathbf{G}_i) \varepsilon_{i'}(\mathbf{q} - \mathbf{G}_i) \int P_{i'}(\mathbf{X}) \times \exp[2\pi i(\mathbf{q} - \mathbf{G}_i) \cdot \mathbf{X}] d\mathbf{X}, \quad (14b)$$

where the sum for  $\mathbf{G}_i$  is taken over all the reciprocal-lattice points for the ordered lattice. The following relations are utilized:

$$\int E_i(\mathbf{r}) E_{i'}(\mathbf{r} + \mathbf{R}_i - \mathbf{X}) d\mathbf{r} = \int \varepsilon_i(\mathbf{q}') \varepsilon_{i'}(\mathbf{q}') \times \exp[-2\pi i \mathbf{q}' \cdot (\mathbf{R}_i - \mathbf{X})] d\mathbf{q}', \quad (15)$$

where  $\varepsilon_i(-\mathbf{q}')$  is replaced by  $\varepsilon_{i'}(\mathbf{q}')$ , because the function  $E_{i'}(\mathbf{r})$  has an inversion centre, and

$$\sum_{\mathbf{r}} \exp[2\pi i(\mathbf{q} - \mathbf{q}' - \mathbf{G}) \cdot \mathbf{R}_i] \rightarrow (1/v_0) \sum_{\mathbf{H}} \delta(\mathbf{q} - \mathbf{q}' - \mathbf{G} - \mathbf{H}) \quad (16)$$

where  $\delta$  is the Dirac delta function, and  $\mathbf{H}$  is a fundamental-lattice vector for the disordered structure.  $\mathbf{G} + \mathbf{H}$  is replaced by  $\mathbf{G}_i$  in equation (14).

If the function  $\varepsilon_i(\mathbf{q} - \mathbf{G}_i)$  is concentrated around the reciprocal-lattice point  $\mathbf{G}_i$  so that the overlapping of the  $\varepsilon_i(\mathbf{q} - \mathbf{G}_i)$ 's around the different superlattice points  $\mathbf{G}_j$  may be small, the interference part of the scattering intensity  $I_{\text{MD}}^i(\mathbf{q})$  in the vicinity of the reciprocal-lattice point  $\mathbf{G}_i$  may be written approximately as

$$I_{\text{MD}}^i(\mathbf{q}) = \frac{m_A m_B}{v_0^2} |f_A - f_B|^2 \sum_{\mathbf{r}} \sum_{\mathbf{r}'} N_i \gamma_{\mathbf{G}_i}^{(tr')} \varepsilon_i(\mathbf{q}_i) \varepsilon_{i'}(\mathbf{q}_i) \times \int P_{i'}(\mathbf{X}) \exp(2\pi i \mathbf{q}_i \cdot \mathbf{X}) d\mathbf{X}, \quad (17)$$

where  $\mathbf{q}_i = \mathbf{q} - \mathbf{G}_i$ ;  $\mathbf{q}_i$  lies quite close to the reciprocal-lattice vector  $\mathbf{G}_i$ . According to the results of a computer simulation by Gehlen & Cohen (1965) and the diffraction theory of Greenholz & Kidron (1970), the

dimension of the domains is about 12 Å (or  $3 \times 3 \times 3$  unit cells) in the case of  $\text{Cu}_3\text{Au}$ . Therefore the assumption mentioned above may be considered to be reasonable in the cases of  $\text{Cu}_3\text{Au}$  and  $\text{CuAu}$  alloys.

### Simple examples for intensity calculations

If microdomains belonging to the same type of order grow in clusters, only the statistical distribution  $P_{ii}(\mathbf{X})$  has a finite value and the other  $P_{i' i'}(\mathbf{X})$  for  $i \neq i'$  vanish. Therefore equation (17) becomes

$$I_{\text{MD}}^i(\mathbf{q}_i) = \frac{m_A m_B}{v_0^2} |f_A - f_B|^2 \sum_{\mathbf{r}} N_i \gamma_{\mathbf{G}_i}^{(ii)} \varepsilon_i^2(\mathbf{q}_i) \times \int P_{ii}(\mathbf{X}) \exp(2\pi i \mathbf{q}_i \cdot \mathbf{X}) d\mathbf{X}. \quad (18)$$

This equation has a maximum at  $\mathbf{q}_i = 0$ , because  $\varepsilon_i(\mathbf{q}_i)$  has its maximum value at  $\mathbf{q}_i = 0$  and  $\gamma_{\mathbf{G}_i}^{(ii)} \geq 0$ , and therefore, correlation between ordered microdomains in antiphase relation must be introduced in order to explain the fine structure of the diffuse scattering shown in Fig. 1.

Another example is given in the following: when microdomains of all the types of order are related to one another by antiphase relations only, such as in the  $\text{Cu}_3\text{Au}$ -type structure,  $I_{\text{MD}}^i(\mathbf{q}_i)$  takes a very simple form; *i.e.*

$$I_{\text{MD}}^i(\mathbf{q}_i) = \frac{m_A m_B}{v_0^2} |f_A - f_B|^2 N_d \varepsilon_i^2(\mathbf{q}_i) \times \sum_{\mathbf{r}} \gamma_{\mathbf{G}_i}^{(i' i')} \int P_{i' i'}(\mathbf{X}) \exp(2\pi i \mathbf{q}_i \cdot \mathbf{X}) d\mathbf{X}, \quad (19)$$

where  $N_d (= \sum_{\mathbf{r}} N_i)$  is the number of microdomains in the crystal. The form factors  $\varepsilon_i(\mathbf{q}_i)$  become the same  $\varepsilon_i(\mathbf{q}_i)$  for all the types. When  $\mathbf{G}_i$  is a superlattice vector,  $\gamma_{\mathbf{G}_i}^{(i' i')}$  takes a negative value for certain type of  $i'$  in antiphase with the first type, as shown in Table 1. Therefore, if  $P_{i' i'}(\mathbf{X})$  takes a large positive value for such pairs of microdomains with the interdomain vector  $\mathbf{X} = \mathbf{X}_0$ ,  $I_{\text{MD}}^i(\mathbf{q}_i)$  may take a negative value just around  $\mathbf{q}_i = 0$ , and a large positive value around  $\mathbf{q}_i$  corresponding to  $\mathbf{q}_i \cdot \mathbf{X}_0 = \frac{1}{2}$ . This explains weakening of the diffuse scattering due to SRO at a superlattice position  $\mathbf{G}_i$  and reinforcement at  $\mathbf{q} = 2\mathbf{k}_F$  around  $\mathbf{G}_i$ .

Table 1.  $\gamma_{\mathbf{G}_i}^{(i' i')}$  for different values of  $i'$  in the  $\text{Cu}_3\text{Au}$ -type structure

$i'$	$\xi_{i'}$	$\mathbf{G}_{100}$	$\mathbf{G}_{010}$	$\mathbf{G}_{110}$
1	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
2	$(\frac{1}{3})a[110]$	$-\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$
3	$(\frac{1}{3})a[011]$	$\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$
4	$(\frac{1}{3})a[101]$	$-\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$

$\xi_{i'}$  is the out-of-step vector with respect to the first-type ordered structure. See Appendix I.

The following equation results from equation (19):

$$\sum_{i'} \gamma_{\mathbf{G}_i}^{(i')} P_{1i'}(\mathbf{X}) = \int_{\text{around } \mathbf{G}_i} \frac{I_{\text{MD}}^i(\mathbf{q}_i)}{(m_A m_B / v_0^2) N_d |f_A - f_B|^2 \varepsilon_1^2(\mathbf{q}_i)} \times \exp(-2\pi i \mathbf{q}_i \cdot \mathbf{X}) d\mathbf{q}_i. \quad (20)$$

The integration of the right-hand side of equation (20) is made only in the vicinity of the superlattice position  $\mathbf{G}_i$ . This equation gives several linear equations associated with the superlattice points in the first Brillouin zone for a disordered lattice, that is, three equations for an ordered lattice as shown in Appendix I. When the number of  $P_{1i'}$ 's for a certain interdomain distance  $\mathbf{X}$  is equal to the number of linear equations, the  $P_{1i'}$ 's can be solved uniquely with equation (20). Even if the former number exceeds the latter, some valuable relations among the  $P_{1i'}(\mathbf{X})$ 's can be obtained by some physical considerations. This subject will be treated in a subsequent paper on specified alloys. We try here a simple calculation for the case of an  $A_3B$ -type structure. If there are finite probabilities  $P_{1i'}(\mathbf{X})$  for the definite interdomain vectors  $\mathbf{X}$  as follows:

$$\begin{aligned} P_{12}(\mathbf{X}) &= P_{14}(\mathbf{X}) = P \\ \text{for } \mathbf{X} &= a(0, X_0, X_0), a(0, \bar{X}_0, X_0), a(0, X_0, \bar{X}_0) \text{ and} \\ & a(0, \bar{X}_0, \bar{X}_0), \\ P_{12}(\mathbf{X}) &= P_{13}(\mathbf{X}) = P \\ \text{for } \mathbf{X} &= a(X_0, 0, X_0), a(\bar{X}_0, 0, X_0), a(X_0, 0, \bar{X}_0) \text{ and} \\ & a(\bar{X}_0, 0, \bar{X}_0), \\ P_{13}(\mathbf{X}) &= P_{14}(\mathbf{X}) = P \\ \text{for } \mathbf{X} &= a(X_0, X_0, 0), a(\bar{X}_0, X_0, 0), a(X_0, \bar{X}_0, 0) \text{ and} \\ & a(\bar{X}_0, \bar{X}_0, 0), \end{aligned} \quad (21)$$

where  $\mathbf{X} = a(0, X_0, X_0)$  stands for  $\mathbf{X} = 0\mathbf{a} + X_0\mathbf{b} + X_0\mathbf{c}$ ,  $|\mathbf{a}| = |\mathbf{b}| = |\mathbf{c}| = a$  being the lattice constant of the cubic crystal lattice.  $I_{\text{MD}}^i(\mathbf{q}_i)$  takes the following values:

$$\begin{aligned} I_{\text{MD}}^i(\mathbf{q}_{100}) &\propto \varepsilon_1^2(\mathbf{q}_{100}) (-P \cos 2\pi h_2 X_0 \cos 2\pi h_3 X_0) \\ & \text{around } \mathbf{G}_{100}, \\ I_{\text{MD}}^i(\mathbf{q}_{010}) &\propto \varepsilon_1^2(\mathbf{q}_{010}) (-P \cos 2\pi h_3 X_0 \cos 2\pi h_1 X_0) \\ & \text{around } \mathbf{G}_{010}, \\ I_{\text{MD}}^i(\mathbf{q}_{110}) &\propto \varepsilon_1^2(\mathbf{q}_{110}) (-P \cos 2\pi h_1 X_0 \cos 2\pi h_2 X_0) \\ & \text{around } \mathbf{G}_{110}, \end{aligned} \quad (22)$$

where the subscripts 1-4 of  $P(\mathbf{X})$  represent the types of order in Fig. 5, and 100, 010 and 110 the superlattice reflexion positions in the case of the  $L1_2$  structure.  $h_1$ ,  $h_2$  and  $h_3$  are continuous variables in reciprocal space, i.e.  $\mathbf{q}_i = h_1\mathbf{a}^* + h_2\mathbf{b}^* + h_3\mathbf{c}^*$ ,  $|\mathbf{a}^*| = |\mathbf{b}^*| = |\mathbf{c}^*|$  being equal to  $(1/a)$ . Thus, it can be seen that the microdomain distribution given in equation (21) causes an intensity modification as expressed in equation (22), which is approximately similar to that around the superlattice reflexion positions in Fig. 1. In the practical case of the  $\text{Cu}_3\text{Au}$  alloy, as shown in Fig. 1, the  $P_{1i'}(\mathbf{X})$ 's must be given as continuous functions of the vector  $\mathbf{X}$ .

## Discussion

The diffraction effects due to crystal distortions (or uniform strains) and atomic displacements (or local strains) are neglected in the present treatment, but it is rather easy to introduce these effects qualitatively. For example, it may be considered, in the case of the  $\text{CuAu}$  alloy, that there exist microdomains of the  $L1_0$  structure deformed tetragonally in a disordered state. Such a crystal distortion gives rise to a peak shift of the diffuse scattering corresponding to the tetragonality with respect to the reciprocal fundamental lattice.

Such peak shifts of diffuse intensities have been observed experimentally for the  $\text{CuAu}$  alloy (Sato, Watanabe & Ogawa, 1962; Hashimoto & Ogawa, 1970).

The disordered region as defined in the CMDM is, in practice, not necessarily perfectly disordered, but the nearest-neighbour atomic pairs of different kinds may be enhanced even in that region because of the presence of the repulsive interaction between ion cores. This effect has not strictly been considered in the present treatment, but the usefulness of the CMDM cannot be underestimated for this reason.

Various models that have so far been proposed are constructed with only the first few  $\alpha_i$  parameters, and therefore they cannot explain the fine structure of the diffuse scattering due to SRO. The introduction of correlations between ordered microdomains in the present CMDM corresponds to consideration of the long-range part of the  $\alpha_i$  parameters. The CMDM is capable of explaining the fine structure observed in the cases of  $\text{Cu}_3\text{Au}$ ,  $\text{CuAu}$  (Sato, Watanabe & Ogawa, 1962; Hashimoto & Ogawa, 1970) and  $\text{Cu}_3\text{Pd}$  (Watanabe, 1959; Oshima & Watanabe, 1973).

The reasonableness of the CMDM is understandable on the basis of the possibility of the existence of microdomains in disordered alloys with SRO, as revealed by the computer-simulation work of Gehlen & Cohen (1965) and the thermodynamical considerations of Moss (1969). According to Gehlen & Cohen, the microstructure computed from  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  in the disordered

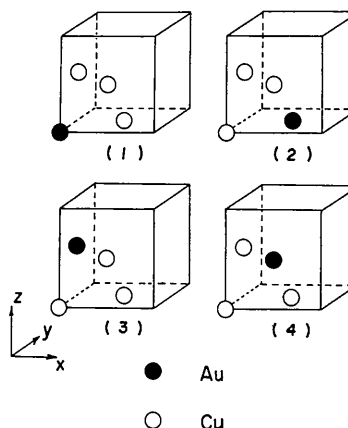


Fig. 5. Four types of ordered lattice  $\text{Cu}_3\text{Au}$ . Open and solid circles represent copper and gold atoms respectively.

Cu<sub>3</sub>Au alloy is described as a random matrix in which ordered regions are embedded. This result shows that, if a set of the  $\alpha_i$  parameters has proper values in the short-range part, there exist microdomains in the SRO alloys. Such interatomic correlations are considered to be caused by very short-range interatomic interactions. However, it has been made clear that the considerably longer-range interaction, due to the Fermi surface effects on the electron energy, plays an important role in the fine structure of the diffuse scattering in a diffraction pattern. Therefore it seems to be reasonable to consider that a microdomain structure is perturbed by the long-range interaction, *i.e.* microdomains correlate with one another in a disordered matrix, and this effect is responsible for the formation of the antiphase relation.

A diffraction study on the isothermal variation of the electron diffraction pattern from Cu<sub>3</sub>Au by Yamaguchi, Watanabe & Ogawa (1962) has shown that in the initial stage of the ordering process, superlattice reflexions appear with a shape similar to the diffuse scattering in the disordered state and the former reflexions become sharper and stronger with increasing annealing time. This phenomenon can be easily understood from the CMDM as follows: an order-disorder transformation, as in Cu<sub>3</sub>Au, proceeds through atomic diffusion. Therefore the ordering in the initial stage advances around the microdomains embedded in a disordered matrix, domain boundaries form, and the domains grow larger and larger. For the reverse case, the disordering process of a perfectly ordered single crystal is considered. The degree of order progressively decreases with rising temperature. When the temperature exceeds  $T_c$ , the ordering is mostly destroyed, and finally microdomains in antiphase relation grow and are arranged by atomic diffusion so as to stabilize the conduction-electron energy.

Finally, it should be understood, according to the CMDM, that the microdomain structure above  $T_c$  is not a remnant of the antiphase domain structure in the partially ordered state, but the latter is just a development of the former.

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#### APPENDIX I

The term 'the type of order' is explained in the case of a Cu<sub>3</sub>Au-type alloy. There are four types of ordered structure depending on which of the four sublattice positions are occupied by gold atoms. This is shown in Fig. 5. If an ordered microdomain is in phase with the structure indicated by (1), (2), (3) or (4) in Fig. 5, we call the type of order of the domain the 1st, 2nd, 3rd or 4th type of order respectively.

#### APPENDIX II

We consider here how the various kinds of shape and size of microdomains are averaged and how the form factor  $\varepsilon_i(\mathbf{q})$  is obtained from the experimental data.

The SRO intensity due to the microdomain structure model, except the interference effect between the domains corresponding to  $I_{LM} + I_{MD}^0$ , is expressed using the Warren SRO parameters as follows:

$$I'_{sro}(\mathbf{q}) = nm_A m_B |f_A - f_B|^2 \sum_i \alpha'_i \exp(2\pi i \mathbf{q} \cdot \mathbf{R}_i) \quad (A1)$$

where  $n$  is the number of atoms in the alloy crystal and the  $\alpha_i$  parameters are denoted as  $\alpha'_i$  for the model without correlations between microdomains. Comparing equation (A1) with  $I'_{sro}(\mathbf{q}) = I_{LM} + I_{MD}^0(\mathbf{q})$  which can be expressed by equations (4) and (11b), we obtain

$$\alpha'_i = \frac{n_r}{n} \delta_{i,0} + \sum_T \frac{N_t}{V} C_i^{(t)} \int E_i(\mathbf{r}) E_i(\mathbf{r} + \mathbf{R}_i) d\mathbf{r}, \quad (A2)$$

where  $V$  equals  $nv_0$ , the volume of the alloy crystal.

The  $\alpha'_i$  parameters may be very close to the true  $\alpha_i$  parameters within the range of small  $|\mathbf{R}_i|$ , because they are not very much affected by pairs of sites belonging to the separated domains within this range. Therefore, we approximate

$$\alpha'_i = \begin{cases} \alpha_i & \text{within the range of small } |\mathbf{R}_i| \\ & \text{(sometimes with a little correction)} \\ 0 & \text{otherwise.} \end{cases} \quad (A3)$$

The shape of the microdomains is considered to be closely related to the symmetry of the type of order, *e.g.* the cubic symmetry for the Cu<sub>3</sub>Au type, the tetragonal symmetry for the CuAu type, *etc.* Therefore, the mean shape function should be different according to the symmetry of the ordered structure for each type of order and orientation of the domains. We consider here the case of the A<sub>3</sub>B-cubic-type structure for simplicity. In this case, equation (A2) is simplified as follows:

$$\alpha_i = \frac{n_r}{n} \delta_{i,0} + \frac{N_d}{V} C_i^{(11)} \int E_1(\mathbf{r}) E_1(\mathbf{r} + \mathbf{R}_i) d\mathbf{r}, \quad (A4)$$

where the mean shape function is represented by  $E_1(\mathbf{r})$ , since the domains of all the types of order are physically equivalent.  $N_d$  is the total number of microdomains in the crystal. By using the property of the Fourier integral in consideration of equation (13), the following equations are obtained:

$$\int E_1^2(\mathbf{r}) d\mathbf{r} = \int \varepsilon_1^2(\mathbf{q}) d\mathbf{q} = (n_d v_0 / N_d) \quad \text{for } l=0, \quad (A5a)$$

$$\int \varepsilon_1^2(\mathbf{q}) \exp(-2\pi i \mathbf{q} \cdot \mathbf{R}_i) d\mathbf{q} = \frac{\alpha'_i}{C_i^{(11)}} \left( \frac{V}{N_d} \right) \quad \text{for } l \neq 0. \quad (A5b)$$

$n_d$  is  $n - n_r$ , and is the number of atoms in the ordered microdomains.  $(n_d v_0 / N_d)$  therefore indicates the

average volume of a microdomain. The inverse of equation (A5) becomes

$$\varepsilon_1^2(\mathbf{q}) = v_0 \left( \frac{V}{N_d} \right) \sum_i \frac{\alpha_i'}{C_i^{(ii)}} \exp(2\pi i \mathbf{q} \cdot \mathbf{R}_i). \quad (\text{A6})$$

Up to equation (A5),  $\varepsilon_1^2(\mathbf{q})$  is defined as a function concentrated only around  $\mathbf{q}=0$ . In equation (A6),  $\varepsilon_1^2(\mathbf{q})$  is given as a periodic function in the fundamental lattice, as the  $\alpha_i'$  parameters are defined only at the direct lattice points. If  $\varepsilon_1^2(\mathbf{q})$  is sufficiently concentrated in the vicinity of a reciprocal-lattice point, the distribution just around  $\mathbf{q}=0$  may be regarded as  $\varepsilon_1^2(\mathbf{q})$  given in equation (A5). Thus, the mean shape function is obtained from the experimental intensity data using equations (A3) and (A6). At this stage, there is still uncertainty in the value of  $N_d$  in (A6). The following consideration will help determine it.

The function  $E_1(\mathbf{r})$  may be regarded as a sort of order parameter according to the definition in equation (6). If each site within a microdomain is occupied by the correct atom for the ordered structure,  $E_1(\mathbf{r})$  becomes unity, as was given in equation (6), and if the degree of order decreases with increasing distance from the centre of the microdomain, it changes from 1 to 0 with increasing distance  $|\mathbf{r}|$ . According to this consideration, the following equation holds:

$$E_1(\mathbf{r}=0) = \int \varepsilon_1(\mathbf{q}) d\mathbf{q} = 1. \quad (\text{A7})$$

Here,  $|\varepsilon_1(\mathbf{q})|$  can be obtained directly from the experimental data using equation (A6), but  $\varepsilon_1(\mathbf{q})$  cannot. In the non-correlation model considered here, however,  $\varepsilon_1^2(\mathbf{q})$  may be approximated by a smooth function such

as a Cauchy, Gaussian, exponential function, *etc.*, and then  $\varepsilon_1(\mathbf{q})$  may be a smooth positive function. In most practical cases,  $\varepsilon_1(\mathbf{q})$  in equation (A7) may be safely replaced by  $|\varepsilon_1(\mathbf{q})|$ . Using  $|\varepsilon_1(\mathbf{q})|$  obtained from equations (A6) and (A7),  $N_d$  is evaluated.

It is inferred from equation (A5a) that  $E_1^2(\mathbf{r})$  represents the distribution of size and shape of microdomains.

## References

- BATTERMAN, B. (1956). Ph. D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass.  
 COWLEY, J. M. (1950). *J. Appl. Phys.* **21**, 24–30.  
 GEHLEN, P. C. & COHEN, J. B. (1965). *Phys. Rev.* **139**, A844–A855.  
 GREENHOLZ, M. & KIDRON, A. (1970). *Acta Cryst.* **A26**, 311–314.  
 GUINIER, A. (1963). *X-Ray Diffraction*, Translated by P. LORRIAN. San Francisco: W. H. Freeman.  
 HASHIMOTO, S. & OGAWA, S. (1970). *J. Phys. Soc. Japan*, **29**, 710–721.  
 MOSS, S. C. (1966). *Local Atomic Arrangements Studied by X-Ray Diffraction*, Edited by J. B. COHEN & J. E. HILLIARD, pp. 95–122. New York: Gordon & Breach.  
 MOSS, S. C. (1969). *Phys. Rev. Lett.* **22**, 1108–1111.  
 OSHIMA, K. & WATANABE, D. (1973). *Acta Cryst.* **A29**, 520–526.  
 SATO, K., WATANABE, D. & OGAWA, S. (1962). *J. Phys. Soc. Japan*, **17**, 1647–1651.  
 WATANABE, D. (1959). *J. Phys. Soc. Japan*, **14**, 436–443.  
 WILSON, A. J. C. (1962). *X-Ray Optics*. New York: John Wiley.  
 YAMAGUCHI, S., WATANABE, D. & OGAWA, S. (1962). *J. Phys. Soc. Japan*, **17**, 1030–1041.

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## Some Neutron Diffraction Experiments on Curved Silicon Crystals

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The diffraction properties of curved silicon crystals, with curvature radii between  $\infty$  and 25 m obtained by microscopic techniques, were investigated by means of a neutron diffractometer. The ratio of neutron reflectivity between plane and curved silicon crystals was measured as a function of the neutron wavelength using different reflecting planes in both Bragg and Laue cases in symmetrical and asymmetrical conditions. The experimental results were interpreted with the results of theoretical investigations on the dynamical theory of diffraction applied to the curved-crystal case. The implications of this work on neutron monochromator design are briefly discussed.

### 1. Introduction

The problem of neutron diffraction by curved crystals has been treated theoretically (Klar & Rusticelli, 1973) by an extension of the dynamical theory for X-ray

diffraction (Taupin, 1964a, b). The aim of this work was to give an experimental contribution in the same field of the physics of neutron diffraction by curved crystals. The ratio of neutron reflectivities between perfect plane crystals and curved crystals with the same