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**A simplified formula for the calculation of the X-ray intensity diffracted by a monodimensionally disordered structure.** By G. ALLEGRA, *Istituto di Chimica Industriale del Politecnico, Piazza Leonardo da Vinci 32, Milano, Italy*

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We have been recently concerned with the calculation of the X-ray intensity diffracted by different models of structures showing disorder with  $s=1$  in the stacking of layers. An example is severely ground  $\alpha$  (Natta *et al.*, 1958) or  $\gamma$  (Natta *et al.*, 1959)  $\text{TiCl}_3$ . In the course of our study, we have found a simplified formula for the calculation of the mean intensity diffracted by a single layer.

Mean diffracted intensity is given by:

$$I_{AV} = \sum_1^r i f^{(i)} V^{(i)2} + \sum_K \sum_1^r \sum_{i,j} \mathbf{V}^{(i)*} \mathbf{V}^{(j)} f^{(i)} f^{(j)} Q_K^{(ij)} + \sum_K \sum_1^r \sum_{i,j} \mathbf{V}^{(j)} \mathbf{V}^{(i)*} f^{(i)} f^{(j)} Q_K^{(ji)*}; \quad (1)$$

where:

- $r$  is the different layers;
- $f^{(i)}$  is the frequency of occurrence of the layer of  $i$ th kind;
- $\mathbf{V}^{(i)}$  is the structure factor of the layer of  $i$ th kind;
- $\mathbf{Q}_K$  is the matrix whose  $(i, j)$  element is given by the product  $P_K^{(ij)} \exp[-i\varphi_K^{(ij)}]$ ,  $P_K^{(ij)}$  being the probability for a layer of the kind  $i$  to be followed by a  $K$ th neighbour of the kind  $j$ , and  $\exp[-i\varphi_K^{(ij)}]$  the corresponding fringe factor.

According to Hendricks & Teller (1942), (1) reduces to:

$$I_{AV} = \sum_1^r i f^{(i)} V^{(i)2} + \sum_1^r \frac{R^{(ii)} Q^{(i)}}{1 - Q^{(i)}} + \sum_1^r i \frac{R^{(ii)*} Q^{(i)*}}{1 - Q^{(i)*}}; \quad (2)$$

where  $Q^{(i)}$  are the eigenvalues of  $\mathbf{Q}_1$ , reduced to diagonal form by the similarity operation  $\mathbf{O}\mathbf{Q}_1\mathbf{O}^{-1}$ , and  $R^{(ii)}$  are the diagonal elements of the matrix  $\mathbf{O}\mathbf{V}\mathbf{F}\mathbf{O}^{-1}$ , with  $\mathbf{V}^{(ij)} = \mathbf{V}^{(i)} \mathbf{V}^{(j)*}$  and  $F^{(ij)} = \delta^{(ij)} f^{(i)}$ .

It may be possible that the matrix  $\mathbf{Q}_1$  cannot be diagonalized, if its eigenvalues are not all different and if  $\mathbf{Q}_1$  is not symmetrical.

A new formula for  $I_{AV}$ , subjected to no conditions of

the above type, and simpler than (2), may be derived from (1) in the following way.

Let  $\mathbf{V}$  be the row vector:

$$|\mathbf{V}^{(1)} \dots \mathbf{V}^{(i)} \dots \mathbf{V}^{(r)}|$$

and  $\tilde{\mathbf{V}}$  the corresponding column vector. Remembering that  $\mathbf{Q}_K = \mathbf{Q}_1^K$ , (1) reduces to:

$$I_{AV} = \sum_1^r i f^{(i)} V^{(i)2} + \sum_K \mathbf{V}\mathbf{F}\mathbf{Q}_K \tilde{\mathbf{V}}^* + \sum_K \mathbf{V}^* \mathbf{F}\mathbf{Q}_K^* \tilde{\mathbf{V}} = \mathbf{V}\mathbf{F} \left\{ \sum_0^K \mathbf{Q}_1^K \right\} \tilde{\mathbf{V}}^* + \mathbf{V}^* \mathbf{F} \left\{ \sum_0^K \mathbf{Q}_1^{K*} \right\} \tilde{\mathbf{V}} - \sum_1^r i f^{(i)} V^{(i)2}. \quad (3)$$

But  $(\mathbf{Q}_1^K)^{(ij)}$ , in the limit of  $K \rightarrow \infty$ , is generally vanishing in whatever statistical structure. Then (3) reduces to:

$$I_{AV} = \mathbf{V}\mathbf{F}(\mathbf{E} - \mathbf{Q}_1)^{-1} \tilde{\mathbf{V}}^* + \mathbf{V}^* \mathbf{F}(\mathbf{E} - \mathbf{Q}_1^*)^{-1} \tilde{\mathbf{V}} - \sum_1^r i f^{(i)} V^{(i)2}. \quad (4)$$

The only lengthy step in the calculation of  $I_{AV}$  through (4) is the evaluation of  $(\mathbf{E} - \mathbf{Q}_1)^{-1}$ ; whereas the calculation of  $I_{AV}$  through (2) requires the diagonalization of  $\mathbf{Q}_1$ , which is not always possible, and the lengthy evaluation of  $\mathbf{O}$ ,  $\mathbf{O}^{-1}$ ,  $\mathbf{O}\mathbf{V}\mathbf{F}\mathbf{O}^{-1}$ .

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**Neutron diffraction by helical spin structures.** By W. C. KOEHLER, *Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.*

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Recently a new class of magnetic structures, the helical spin structures, has been discussed theoretically (Yoshimori, 1959; Villain, 1959), and a number of experimental examples, for instance in  $\text{MnAu}_2$  (Herpin *et al.*, 1959) and in metallic holmium (Koehler *et al.*, 1960) has been discovered in neutron diffraction experiments. A simple helical structure may be described as follows: let the ideal lattice sites of the chemical unit cell be described by  $\mathbf{r}_k + \mathbf{A}_L$  and let us suppose that at each such lattice site is found a magnetic moment  $\mu \hat{K}_k^L$  such

that all moments make the same constant projection on some crystal direction defined by the unit vector  $\hat{u}_3$ ; that is to say, the moment directions are assumed to be given by

$$\hat{K}_k^L = \cos \beta \hat{u}_3 + \sin \beta \hat{u}_k^L, \quad (1)$$

where  $\hat{u}_k^L$  is a unit vector normal to  $\hat{u}_3$  and  $\beta$  is the constant angle between the moment directions and  $\hat{u}_3$ . It is further assumed that the directions  $\hat{u}_k^L$  are described by

$$\hat{u}_k^L = [(\hat{u}_1 - i\hat{u}_2)/2 \exp i2\pi\tau \cdot (\mathbf{r}_k + \mathbf{A}_L) + \text{C.C.}] \quad (2)$$

in which  $\boldsymbol{\tau}$  is a reciprocal lattice vector normal to planes of parallel moments and which defines the screw axis of the structure. The direction  $\hat{u}_3$  may be called the axis of moment rotation,  $\hat{u}_1$  and  $\hat{u}_2$  are unit vectors in the plane normal to  $\hat{u}_3$ .

It is the purpose of this note to point out that the intensity formulae necessary for the interpretation of neutron diffraction data for such helical type structures may be simply derived by the application of the general theory of X-ray diffraction in disordered lattices as given by Zachariasen (1945).

We shall use Zachariasen's notation throughout, and for completeness reproduce here a few of his fundamental definitions, noting first of all that the magnetic scattering amplitude, a vector, to be associated with the lattice site  $\mathbf{r}_k + \mathbf{A}_L$  may be written

$$p\mathbf{q}_k^L = p[(\hat{s} \cdot \hat{K}_k^L)\hat{s} - \hat{K}_k^L], \quad (3)$$

where  $p$  is as usual  $(e^2\gamma/2mc^2)\mu f_m$  in which  $f_m$  is the magnetic form factor and all other symbols have their customary significance and where  $\hat{s}$  is the unit scattering vector. We define a mean amplitude for the set  $k$  by

$$\bar{\mathbf{g}}_k = 1/N \sum_L p\mathbf{q}_k^L \quad (4)$$

and a fluctuation, or disorder, for the site  $\mathbf{r}_k + \mathbf{A}_L$  by

$$\boldsymbol{\varphi}_k^L = p\mathbf{q}_k^L - \bar{\mathbf{g}}_k. \quad (5)$$

It will be noted that the disorders  $\boldsymbol{\varphi}_k^L$  are doubly periodic corresponding to the supposition that there exist planes normal to  $\boldsymbol{\tau}$  in which the moments are parallel. Since the mean value of the disorder of the set  $k$  must vanish we shall assume for the balance of this discussion that

$$1/N \sum_L \hat{u}_k^L = 0. \quad (6)$$

This condition obviously fails if  $\boldsymbol{\tau} = 2\pi\mathbf{B}_H$  but such a case is of no interest here. We have then the relations

$$\bar{\mathbf{g}}_k = p \cos \beta [(\hat{s} \cdot \hat{u}_3)\hat{s} - \hat{u}_3], \quad \boldsymbol{\varphi}_k^L = p \sin \beta [(\hat{s} \cdot \hat{u}_k^L)\hat{s} - \hat{u}_k^L]. \quad (7)$$

The intensity of scattering from a small disordered crystallite is (Zachariasen's equations 4.203 and 4.204)  $I = J_1 + J_2$

$$J_1 = |\bar{\mathbf{F}}|^2 \sum_{L, L'} \exp i\mathbf{s} \cdot (\mathbf{A}_L - \mathbf{A}_{L'})$$

$$J_2 = \sum_{L, L'} \exp i\mathbf{s} \cdot (\mathbf{A}_L - \mathbf{A}_{L'}) \sum_{kk'} \boldsymbol{\varphi}_{kk'}^{L-L'} \exp i\mathbf{s} \cdot (\mathbf{r}_k - \mathbf{r}_{k'}), \quad (8)$$

where

$$\boldsymbol{\varphi}_{kk'}^M = 1/N \sum_L \boldsymbol{\varphi}_k^L \cdot (\boldsymbol{\varphi}_{k'}^{L-M})^*$$

is the mean value of the products of the disorders at sites separated by  $\mathbf{r}_k - \mathbf{r}_{k'} + \mathbf{A}_M$ .

The mean structure factor  $\bar{\mathbf{F}}$  becomes, if  $\mathbf{F}_L$  is the structure factor of the unit cell with origin at  $\mathbf{A}_L$

$$\bar{\mathbf{F}} = 1/N \sum_L \mathbf{F}_L = \sum_k \bar{\mathbf{g}}_k \exp i\mathbf{s} \cdot \mathbf{r}_k \quad (9)$$

and  $J_1$  of equation (8) above is

$$J_1 = p^2 \cos^2 \beta \sin^2 \Theta |R|^2 \prod_i \sin^2 \frac{1}{2} \mathbf{s} \cdot N_i \mathbf{a}_i / \sin^2 \frac{1}{2} \mathbf{s} \cdot \mathbf{a}_i \quad (10)$$

in which  $\Theta$  is the angle between the scattering vector and the spin rotation axis  $\hat{u}_3$  and

$$R = \sum_k \exp i2\pi \mathbf{B}_H \cdot \mathbf{r}_k$$

may be termed the geometrical structure factor of the chemical unit cell. It is clear that  $J_1$ , having its maxima in the exact Laue-Bragg directions for which  $\mathbf{s} = 2\pi\mathbf{B}_H$ , corresponds to the usual case of scattering by a ferromagnetic material.

The disorder scattering  $J_2$  depends upon the quantities  $\boldsymbol{\varphi}_{kk'}^M$  which for this case take the simple form

$$\boldsymbol{\varphi}_{kk'}^M = \frac{1}{4} p^2 \sin^2 \beta (1 + \cos^2 \Theta) [\exp i2\pi \boldsymbol{\tau} \cdot (\mathbf{r}_k - \mathbf{r}_{k'} + \mathbf{A}_M) + \text{C.C.}] \quad (11)$$

from which

$$J_2 = \frac{1}{4} p^2 \sin^2 \beta (1 + \cos^2 \Theta) \times \sum_{L, L', k, k'} \exp i(\mathbf{s} + 2\pi \boldsymbol{\tau}) \cdot (\mathbf{r}_k - \mathbf{r}_{k'} + \mathbf{A}_L - \mathbf{A}_{L'}) + \exp i(\mathbf{s} - 2\pi \boldsymbol{\tau}) \cdot (\mathbf{r}_k - \mathbf{r}_{k'} + \mathbf{A}_L - \mathbf{A}_{L'}) .$$

The first double sum on  $L, L'$  vanishes unless  $\mathbf{s} + 2\pi \boldsymbol{\tau} = 2\pi\mathbf{B}_H$ , the second unless  $\mathbf{s} - 2\pi \boldsymbol{\tau} = 2\pi\mathbf{B}_H$ , the sums over  $kk'$  become simply

$$|\sum_k \exp i2\pi \mathbf{B}_H \cdot \mathbf{r}_k|^2 = |R|^2$$

and the disorder scattering  $J_2$  reduces to

$$J_2^\pm = \frac{1}{4} p^2 \sin^2 \beta (1 + \cos^2 \Theta) |R|^2 \prod_i \frac{\sin^2 \frac{1}{2} (\mathbf{s} \pm 2\pi \boldsymbol{\tau}) \cdot N_i \mathbf{a}_i}{\sin^2 \frac{1}{2} (\mathbf{s} \pm 2\pi \boldsymbol{\tau}) \cdot \mathbf{a}_i} . \quad (12)$$

The disorder scattering thus manifests itself in two equally spaced satellites of the allowed nuclear reflections which are found on reciprocal lattice rows parallel to  $\boldsymbol{\tau}$ . It is noteworthy that there are no angles  $\Theta$  for which the satellite intensities vanish which fact provides a (negative) test for the helical structure. The magnitude of  $\boldsymbol{\tau}$  gives, obviously, a measure of the interplanar turn angle.

If the fluctuations  $\boldsymbol{\varphi}_k^L$  and the quantities  $\boldsymbol{\varphi}_{kk'}^M$  may be expanded in Fourier series then more general types of magnetic structures are amenable to interpretation by expressions analogous to Zachariasen's equations 4.214 and 4.215.

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