

given in equation (9). While this should offer a reasonable first approximation for the included TDS correction (but not the intensity distribution), its accuracy for weaker reflections and normal scans is open to serious question when there are appreciable differences between neighboring structure factors (such as in NaCl, for example) because of the uncertainty in any large negative contributions from 'other' reciprocal lattice points. An extension to non-cubic materials should also be possible using the relations derived by Rouse & Cooper (1969), but the results should be considerably more complicated. Finally, our study was also limited to one-phonon scattering. Calculations based on simple models (Paskin, 1959; Borie, 1961) show that the neglected  $n$ -phonon TDS varies as  $(2M)^n/n!$  so our calculated intensity distribution can give a good estimate of the total TDS only if  $2M$  is small. The two-phonon and higher order TDS distributions appear to peak much less sharply than does the one-phonon TDS, so their contribution to an included TDS correction should be much smaller, but there has not yet been any specific calculation of these quantities. Thus, if the one-phonon included TDS correction is large, the neglect of the higher-order terms must be recognized to be a possible significant source of error.

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## Application of Representation Analysis to the Magnetic Structure of Nickel Chromite Spinel

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The magnetic structure of the tetragonal nickel chromite spinel ( $a_0 = 5.76$ ;  $c = 8.50$  Å) has been solved by representation analysis in space group  $I4_1/amd$ . Magnetic reflexions decompose into two sets; (a) ferrimagnetic ones, produced by a Néel mode along the  $x$ -axis and belonging to the two-dimensional  $\Gamma_{5g}$  representation of wave vector  $\mathbf{k} = [000]$ ; (b) antiferromagnetic reflexions produced by non-colinear antiferromagnetic  $y$  and  $z$  modes belonging to a two-dimensional representation of wave vector  $\mathbf{k} = [001]$ . The Shubnikov groups of the ferri- and antiferromagnetic modes considered separately are  $Imm'a'$  and  $I_p2'2'_1$  respectively. Their intersection has the very low symmetry  $P2'_y$ . The antiferromagnetic mode of Ni (in 000 and  $0\frac{1}{2}\frac{1}{2}$ ) has only  $y$  components ( $S_y = 0.58$ ). The chromium spins decompose into two sets: Cr<sub>I</sub> (in  $0\frac{1}{4}\frac{3}{8}$  and  $\frac{1}{4}\frac{1}{8}\frac{1}{8}$ ) has  $y$  and  $z$  components ( $S_y = +0.73$  for the former and  $-0.73$  for the latter atom,  $S_z = -0.45$ ); Cr<sub>II</sub> (in  $\frac{1}{4}\frac{1}{2}\frac{1}{8}$  and  $\frac{1}{4}0\frac{3}{8}$ ) has only  $z$  components ( $S_z = 0.86$ ). The total spins are (Ni) = 1.0 and (Cr) = 1.11, and the moment values are  $\mu(\text{Ni}) = 2.0 \mu_B$ ;  $\mu(\text{Cr}) = 2.22 \mu_B$ . The figures are computed from neutron diffraction data given by Prince in 1961. An equivalent model (magnetic twin) has ferrimagnetism along  $Oy$  and antiferromagnetic  $x$  and  $z$  modes. Magnetic interactions are highly anisotropic.

## Introduction

$\text{NiCr}_2\text{O}_4$  is a normal cubic spinel ( $Fd3m-O_h^7$  above  $T_1 = 310^\circ\text{K}$  and becomes tetragonal below  $T_1$  (De-lorme, 1955; Lotgering, 1956) with  $a_0 = 5.76$ ,  $c_0 = 8.50$

Å. It is generally admitted that the space group of the tetragonal phase is  $I4_1/amd-D_{4h}^{19}$  (Prince, 1961) with

4Ni in 4(a): 000 (1);  $0\frac{1}{2}\frac{1}{2}$  (2);  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  (3);  $\frac{1}{2}0\frac{3}{4}$  (4)  
 8Cr in 8(d):  $0\frac{1}{4}\frac{3}{8}$  (1);  $\frac{1}{4}\frac{1}{2}\frac{1}{8}$  (2);  $\frac{1}{4}\frac{1}{8}\frac{1}{8}$  (3);  $\frac{1}{4}0\frac{3}{8}$  (4)

plus those noted (5), (6), (7) and (8), resulting from the translation  $\mathbf{t} = \frac{1}{2}\frac{1}{2}\frac{1}{2}$  from the preceding ones. 16 oxygen atoms are in 16 (*h*) with parameters  $x=0$ ,  $y=0.239$ ,  $z=0.392$ . A neutron diffraction study at 77, and 4.2°K by Prince (1961) revealed at the lower temperature a considerable increase of the cubic 111 or tetragonal 101 line which corresponds to classical Néel ferrimagnetism, but in addition new lines with the (tetragonal) indices 100, 111 and 201 appear. No satisfactory structure model was found however (Prince, 1961). We thought that representation analysis of possible magnetic modes as described by one of the authors (Bertaut, 1968, 1970) should show its usefulness here. The idea of the method is that the number of possible magnetic modes in a given symmetry is limited. These symmetry-compatible modes are the building stones for the magnetic structure models. The observed intensities are compared with the calculated model intensities. As in crystallography, one starts with the highest possible symmetry. [Only if no fit is obtained in a given symmetry, one proceeds by a systematic symmetry descent until a satisfactory agreement is obtained. See, for example, (Fruchart, Bertaut, Sayetat, Nasr Eddine, Fruchart & Sénateur, 1970).] Our discussion closely follows Bertaut (1970). The wave-vectors  $\mathbf{k}$ , characteristic for the magnetic translation groups, are taken from the diffraction experiment (§ 2) and the irreducible group representations are derived for them (§ 3). As an example, the permutation representations induced by point transformations on the crystallographic sites 4(*a*) and 8(*d*) are completely reduced (§ 4). With this information, the irreducible representations to which the magnetic modes belong are simply determined in § 5 and the basis vectors depicting the magnetic modes are found by the projection operator technique (§ 6). The general form of magnetic intensities is expressed and compared to experimental data in § 7. Two equivalent models (twins) are constructed and found to be in good agreement with observation (§ 8). Finally the Shubnikov symmetry (§ 9) and magnetic interactions are briefly discussed (§ 10).

## 2. Wave vectors

Magnetic translation lattices are intimately connected with the concept of wave vectors  $\mathbf{k}$ . If  $\mathbf{t}$  is a crystallographic lattice translation,  $\exp(2\pi i \mathbf{k} \cdot \mathbf{t}) = +1$  means that it is also a magnetic lattice translation while  $\exp(2\pi i \mathbf{k} \cdot \mathbf{t}) = -1$  means that  $\mathbf{t}$  is a magnetic anti-translation. As in ordinary crystallography, the magnetic translation lattices and the corresponding wave vectors are found from extinction rules (Bertaut, 1970). In the present case we have to do with two invariant wave vectors, namely  $\mathbf{k}_1 = 0$  and  $\mathbf{k}_2 = [001]$ .  $\mathbf{k}_1$  corresponds to the ferrimagnetic mode for which the indices *hkl* of non-zero reflexions are such that  $h+k+l=2n$ . Thus the lattice *I* is conserved, *i.e.*  $\exp 2\pi i \mathbf{k}_1 \cdot \mathbf{t} = 1$  for  $\mathbf{t} = \frac{1}{2}\frac{1}{2}\frac{1}{2}$ .  $\mathbf{k}_2 = [001]$  corresponds to the above mentioned new lines for which obviously  $h+k+l=2n+1$ . One

has  $\exp(2\pi i \mathbf{k} \cdot \mathbf{t}) = -1$  for  $\mathbf{k} = \mathbf{k}_2$  and  $\mathbf{t} = \frac{1}{2}\frac{1}{2}\frac{1}{2}$ . The corresponding antcentred magnetic lattice is noted  $I_p$  by Opechowski & Guccione (1965) and  $P_I$  by Belov, Neronova & Smirnova (1965).

There are two possibilities to be investigated. The magnetic structure may be the superposition of a ferrimagnetic mode and an antiferromagnetic mode (in which the Ni and Cr sublattices are separately antiferromagnetic). Then, for a given spin, the components belonging to different representations, *i.e.* to the ferrimagnetic and to the antiferromagnetic mode must be orthogonal.

The other possibility is that two magnetic phases are present, a ferrimagnetic and an antiferromagnetic one.

## 3. Irreducible representations

We use the elegant method devised by Olbrychski (1963) considering only relations between generators.  $(\alpha|\tau_\alpha)$  is a space group operation where  $\alpha$  is a rotation (proper or improper) and  $\tau_\alpha$  is the associated translation, fractional for screw axes and glide planes and equal to a lattice translation for the other symmetry elements. We choose the following generators: a fourfold screw axis  $4_1$  in  $\frac{1}{4}\frac{1}{4}z$ , a twofold rotation axis  $2_x$  in  $x\frac{1}{4}\frac{1}{8}$ , an inversion centre  $\bar{1}$  in  $0\frac{1}{4}\frac{1}{8}$  and the translation  $\mathbf{t} = \frac{1}{2}\frac{1}{2}\frac{1}{2}$ . The group operations can be written

$$4_1 = (4_z|\tau); 2_x = (2_x|\tau); \bar{1} = (\bar{1}|\tau); \mathbf{t} = (1|\mathbf{t}). \quad (3-1)$$

Here  $\tau = 0\frac{1}{4}\frac{1}{4}$ ;  $4_z$ ,  $2_x$ ,  $\bar{1}$  and 1 are the  $3 \times 3$  matrices

$$4_z = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}; \quad 2_x = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\bar{1} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}; \quad 1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (3-2)$$

*Remark*—According to the *International Tables for X-ray Crystallography* (1969)  $4_1$  is here a clockwise screw axis which sends point *xyz* to *y*,  $\frac{1}{2} - x$ ,  $z + \frac{1}{4}$ . This explains why the matrix  $4_z$  above has not the conventional form (which corresponds to an anticlockwise rotation).

Using the well known relation  $(\alpha|\tau_\alpha)(\beta|\tau_\beta) = (\alpha\beta|\alpha\tau_\beta + \tau_\alpha)$ , the following relations between generators are found:

$$(4_1)^4 = (1|001); \bar{1}^2 = (1|001); (2_x)^2 = (1|000)$$

$$(4_1 2_x)^2 = (2_x 4_1)^2 = (1|000); 2_x \bar{1} = \bar{1} 2_x$$

$$4_1 \bar{1} = (1|\frac{1}{2}\frac{1}{2}\frac{1}{2}) \bar{1} 4_1. \quad (3-3)$$

In these relations the translational parts are 000, 001 and  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . Their matrix representative is the unit matrix for the wave vector  $\mathbf{k}_1 = [000]$ . For the wave vector  $\mathbf{k}_2 = [001]$  the matrix representative is still +1 for the translations 000 and 001, but -1 for  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . Denoting the matrix representative of  $(\cdot|\cdot)$  by  $D(\cdot|\cdot)$ , one has

$$D((4_1)^4) = D(I^2) = D((2_x)^2) = D((4_1 2_x)^2) = D((2_x 4_1)^2) = 1$$

$$D(I 2_x) = D(2_x I) \quad (3-4)$$

as well for  $k_1$  as for  $k_2$ .

Only the last relation of (3-3) gives rise to a significant difference. One has indeed

$$D(4_1 \cdot I) = D(I \cdot 4_1) \text{ for } k_1 \quad (3-5)$$

but

$$D(4_1 \cdot I) = -D(I \cdot 4_1) \text{ for } k_2. \quad (3-6)$$

The non-commutation of  $4_1$  and  $I$  in (3-6) implies that for  $k_2 = [001]$  there cannot be any one-dimensional irreducible representation. It is also obvious that for  $k_1 = [000]$  the irreducible representations are the same as those well known for the point group  $D_{4h} = 4/mmm$  we reproduce for convenience in Table 1.

*Remark* – The operation  $4_1 2_x I$  corresponds to the glide plane  $d$  in the group symbol  $I4_1/amd$ . One finds  $(4_1 2_x I)^2 = (1|\frac{1}{2}\frac{1}{2}\frac{1}{2})$  and for  $k_2 = [001]$  one has  $D((4_1 2_x I)^2) = -1$ . This last relation is however not independent. One has indeed:

$$(4_1 2_x I)^2 = 4_1 2_x I 4_1 2_x I = 4_1 I 2_x 4_1 2_x I$$

$$= -I 4_1 2_x 4_1 2_x I = -I (4_1 2_x)^2 I = -I^2 = -1. \quad (3-7)$$

By Olbrychski's identification procedure, (cf. Bertaut, 1968) we find matrices for the generators and end up with the four non-equivalent irreducible representations shown in Table 2. One checks that there are no other ones from the rule  $g = \sum_v d_v^2 = 16 = 2^2 + 2^2 + 2^2 + 2^2$

where  $g$  is the number of elements (translations excluded) and  $d_v$  the dimension of the irreducible representation. These are of two kinds; in  $\Gamma_1^+$  and  $\Gamma_1^-$  the matrix representatives of  $4_1$  and  $2_x$  commute; in  $\Gamma_2^+$  and  $\Gamma_2^-$  they do not.

As a first application we study the reduction of the permutation representation  $\Gamma^{\text{perm}}$ , induced by the sites  $4(a)$  (Ni) and  $8(d)$  (Cr). The results of this reduction will be needed later.

#### 4. Permutation representations and their reduction

*4(a) positions (Ni)*

The fourfold screw axis  $4_1$  in  $\frac{1}{4}z$  sends point 1 in 000 to point 2 in  $0\frac{1}{2}\frac{1}{2}$ , point 2 to point 3 in  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  and so on. This permutation of points can be represented by a matrix equation

$$(4_1) \begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \end{bmatrix} = \begin{bmatrix} . & 1 & . & . \\ . & . & 1 & . \\ . & . & . & 1 \\ 1 & . & . & . \end{bmatrix} \begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \end{bmatrix} = \begin{bmatrix} 2 \\ 3 \\ 4 \\ 1 \end{bmatrix}. \quad (4-1)$$

Table 1. Irreducible representations of  $I4_1/amd-D_{4h}^{19}$  for  $k=[000]$

	1	4 <sub>1</sub>	4 <sub>1</sub> <sup>2</sup>	4 <sub>1</sub> <sup>3</sup>	2 <sub>x</sub>	4 <sub>1</sub> 2 <sub>x</sub>	4 <sub>1</sub> <sup>2</sup> 2 <sub>x</sub>	4 <sub>1</sub> <sup>3</sup> 2 <sub>x</sub>	
$\Gamma_1$	1	1	1	1	1	1	1	1	z
$\Gamma_2$	1	1	1	1	-1	-1	-1	-1	
$\Gamma_3$	1	-1	1	-1	1	-1	1	-1	
$\Gamma_4$	1	-1	1	-1	-1	1	-1	1	
$\Gamma_5$	$\begin{pmatrix} 1 & . \\ . & i \end{pmatrix}$	$\begin{pmatrix} i & . \\ . & -i \end{pmatrix}$	$\begin{pmatrix} -1 & . \\ . & -1 \end{pmatrix}$	$\begin{pmatrix} -i & . \\ . & i \end{pmatrix}$	$\begin{pmatrix} . & 1 \\ 1 & . \end{pmatrix}$	$\begin{pmatrix} . & i \\ -i & . \end{pmatrix}$	$\begin{pmatrix} . & -1 \\ -1 & . \end{pmatrix}$	$\begin{pmatrix} . & -i \\ i & . \end{pmatrix}$	x, y

Only eight operations are listed. The inversion is represented by +1 for the representations  $\Gamma_{jg}(j=1, 2, 3, 4, 5)$  and -1 for the representations  $\Gamma_{ju}(j=1, 2, 3, 4, 5)$ . The translation  $t=\frac{1}{2}\frac{1}{2}\frac{1}{2}$  is represented by the unit matrix +1. The representation  $\Gamma_5$  can be made real.

$$\Gamma_{5\text{real}} \begin{pmatrix} 1 & . \\ . & 1 \end{pmatrix} \begin{pmatrix} . & 1 \\ -1 & . \end{pmatrix} \begin{pmatrix} -1 & . \\ . & -1 \end{pmatrix} \begin{pmatrix} . & -1 \\ i & . \end{pmatrix} \begin{pmatrix} . & 1 \\ i & . \end{pmatrix} \begin{pmatrix} 1 & . \\ . & -1 \end{pmatrix} \begin{pmatrix} . & -1 \\ -i & . \end{pmatrix} \begin{pmatrix} -1 & . \\ . & i \end{pmatrix}$$

Table 2. Irreducible representations of  $I4_1/amd$  for  $k=[001]$

	1	4 <sub>1</sub>	4 <sub>1</sub> <sup>2</sup>	4 <sub>1</sub> <sup>3</sup>	2 <sub>x</sub>	4 <sub>1</sub> 2 <sub>x</sub>	4 <sub>1</sub> <sup>2</sup> 2 <sub>x</sub>	4 <sub>1</sub> <sup>3</sup> 2 <sub>x</sub>
$\Gamma_1^+$ and $\Gamma_1^-$	$\begin{pmatrix} 1 & . \\ . & i \end{pmatrix}$	$\begin{pmatrix} i & . \\ . & -i \end{pmatrix}$	$\begin{pmatrix} -1 & . \\ . & -1 \end{pmatrix}$	$\begin{pmatrix} -i & . \\ . & i \end{pmatrix}$	$\begin{pmatrix} . & 1 \\ 1 & . \end{pmatrix}$	$\begin{pmatrix} . & i \\ -i & . \end{pmatrix}$	$\begin{pmatrix} . & -1 \\ -1 & . \end{pmatrix}$	$\begin{pmatrix} . & -i \\ i & . \end{pmatrix}$
$\Gamma_2^+$ and $\Gamma_2^-$	$\begin{pmatrix} 1 & . \\ . & i \end{pmatrix}$	$\begin{pmatrix} 1 & . \\ . & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & . \\ . & i \end{pmatrix}$	$\begin{pmatrix} 1 & . \\ . & i \end{pmatrix}$	$\varepsilon \begin{pmatrix} 1 & . \\ . & i \end{pmatrix}$	$\varepsilon \begin{pmatrix} 1 & . \\ . & -1 \end{pmatrix}$	$\varepsilon \begin{pmatrix} 1 & . \\ . & i \end{pmatrix}$	$\varepsilon \begin{pmatrix} 1 & . \\ . & -1 \end{pmatrix}$
	1	4 <sub>1</sub> · $\bar{I}$	4 <sub>1</sub> <sup>2</sup> · $\bar{I}$	4 <sub>1</sub> <sup>3</sup> · $\bar{I}$	2 <sub>x</sub> $\bar{I}$	4 <sub>1</sub> 2 <sub>x</sub> $\bar{I}$	4 <sub>1</sub> <sup>2</sup> 2 <sub>x</sub> $\bar{I}$	4 <sub>1</sub> <sup>3</sup> 2 <sub>x</sub> $\bar{I}$
$\Gamma_1^+$ and $\Gamma_1^-$	$\eta \begin{pmatrix} . & 1 \\ i & . \end{pmatrix}$	$\eta \begin{pmatrix} . & i \\ -i & . \end{pmatrix}$	$\eta \begin{pmatrix} . & -1 \\ -1 & . \end{pmatrix}$	$\eta \begin{pmatrix} . & -i \\ i & . \end{pmatrix}$	$\eta \begin{pmatrix} 1 & . \\ . & i \end{pmatrix}$	$\eta \begin{pmatrix} i & . \\ . & -i \end{pmatrix}$	$\eta \begin{pmatrix} -1 & . \\ . & -1 \end{pmatrix}$	$\eta \begin{pmatrix} -i & . \\ . & i \end{pmatrix}$
$\Gamma_2^+$ and $\Gamma_2^-$	$\begin{pmatrix} . & 1 \\ i & . \end{pmatrix}$	$\begin{pmatrix} . & 1 \\ -1 & . \end{pmatrix}$	$\begin{pmatrix} . & 1 \\ i & . \end{pmatrix}$	$\begin{pmatrix} . & 1 \\ -1 & . \end{pmatrix}$	$\varepsilon \begin{pmatrix} . & 1 \\ i & . \end{pmatrix}$	$\varepsilon \begin{pmatrix} . & 1 \\ -1 & . \end{pmatrix}$	$\varepsilon \begin{pmatrix} . & 1 \\ i & . \end{pmatrix}$	$\varepsilon \begin{pmatrix} . & 1 \\ -1 & . \end{pmatrix}$

Here for  $\Gamma_1^+$   $\eta = +1$ ; for  $\Gamma_1^-$   $\eta = -1$   
for  $\Gamma_2^+$   $\varepsilon = +1$ ; for  $\Gamma_2^-$   $\varepsilon = -1$ .

A real representation equivalent to  $\Gamma_1^+$  and  $\Gamma_1^-$ , is found when replacing  $4_1 = \begin{pmatrix} i & . \\ . & -i \end{pmatrix}$  by  $4_1 = \begin{pmatrix} . & 1 \\ -1 & . \end{pmatrix}$ .

The translation  $t=\frac{1}{2}\frac{1}{2}\frac{1}{2}$  is represented by  $t = \begin{pmatrix} -1 & . \\ . & -1 \end{pmatrix}$ .

Thus the matrices  $(4_1)$  and correspondingly  $(2_x)$ ,  $(\bar{1})$ ,  $(t)$ , (4-2) are the generators of a permutation representation  $\Gamma^{\text{perm}}$  which has 32 elements, corresponding to the following operations:  $e$ ,  $4_1$ ,  $4_1^2$ ,  $4_1^3$ ;  $2_x$ ,  $4_1 2_x$ ,  $4_1^2 2_x$ ,  $4_1^3 2_x$ ;  $\bar{1}$ ,  $4_1 \bar{1}$ ,  $4_1^2 \bar{1}$ ,  $4_1^3 \bar{1}$ ;  $2_x \bar{1}$ ,  $4_1 2_x \bar{1}$ ,  $4_1^2 2_x \bar{1}$ ,  $4_1^3 2_x \bar{1}$  plus the sixteen operations obtained by multiplying the preceding ones with the translation  $t$  (which sends point 1 to 3, point 2 to 4 and *vice versa*). All the operations are understood *modulo* a lattice translation  $l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3$  ( $l_1, l_2, l_3$  integer numbers).

$$(4_1) = \begin{pmatrix} . & 1 & . & . \\ . & . & 1 & . \\ . & . & . & 1 \\ 1 & . & . & . \end{pmatrix}; (2_x) = \begin{pmatrix} . & 1 & . & . \\ 1 & . & . & . \\ . & . & . & 1 \\ . & . & 1 & . \end{pmatrix} = (\bar{1}); (t) = \begin{pmatrix} . & . & 1 & . \\ . & . & . & 1 \\ 1 & . & . & . \\ . & 1 & . & . \end{pmatrix} \quad (4-2)$$

From the generating matrices (4-2) the 32 matrices of  $\Gamma^{\text{perm}}$  may be constructed and the characters evaluated. Non-zero characters correspond to points conserved in the permutation, *i.e.* to site symmetry elements:

$$\begin{aligned} \chi(e) &= \chi(2_x \bar{1}) = \chi(t 4_1^2) = \chi(t 4_1^2 2_x \bar{1}) = 4 \\ \chi(4_1 2_x) &= \chi(4_1 \bar{1}) = \chi(t 4_1 2_x) = \chi(t 4_1 \bar{1}) = 2 \\ \chi(4_1^3 2_x) &= \chi(4_1^3 \bar{1}) = \chi(t 4_1^3 2_x) = \chi(t 4_1^3 \bar{1}) = 2. \end{aligned} \quad (4-3)$$

The number of times  $a_v$  an irreducible representation  $\Gamma_v$  is contained in  $\Gamma^{\text{perm}}$  is given by

$$a_v = 1/g \sum_T \chi^{(v)}(T)^* \chi(T)$$

and it is found that the irreducible representations for both vectors  $\mathbf{k}_1 = [000]$  and  $\mathbf{k}_2 = [001]$  are needed. Using Tables 1 and 2 and relations (4-3) one has

$$\Gamma^{\text{perm}}(\text{Ni}) = \Gamma_{1g}(\mathbf{k}_1) + \Gamma_{4u}(\mathbf{k}_1) + \Gamma_1^+(\mathbf{k}_2). \quad (4-4)$$

#### 8(d) positions (Cr)

The atoms being numbered as in the introduction, the generating matrices of  $\Gamma^{\text{perm}}$  of dimension eight have the following form

$$(4_1) = \begin{pmatrix} A & O \\ O & A \end{pmatrix}; (2_x) = \begin{pmatrix} B & O \\ O & B \end{pmatrix}; (\bar{1}) = \begin{pmatrix} C & D \\ D & C \end{pmatrix}; (t) = \begin{pmatrix} O & E \\ E & O \end{pmatrix}. \quad (4-5)$$

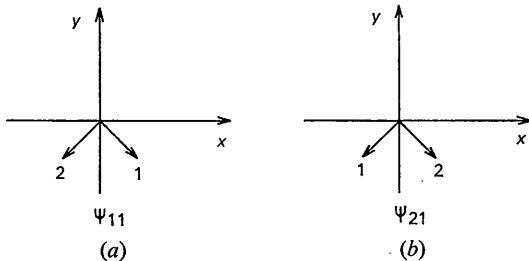


Fig. 1. Graphical representations of modes in  $F_2^-$ . (a)  $\psi_{11x}$  is maximal:  $\psi_{21} = 0$ . (b)  $\psi_{21}$  is maximal and  $\psi_{11} = 0$  [cf. equation (6-4)].

Here  $A, B, C, D, E, O$  are  $4 \times 4$  matrices

$$A = \begin{pmatrix} . & 1 & . & . \\ . & . & 1 & . \\ . & . & . & 1 \\ 1 & . & . & . \end{pmatrix}; B = \begin{pmatrix} 1 & . & . & . \\ . & . & . & 1 \\ . & . & 1 & . \\ . & 1 & . & . \end{pmatrix}$$

$$C = \begin{pmatrix} 1 & . & . & . \\ . & . & . & . \\ . & . & 1 & . \\ . & . & . & . \end{pmatrix}; D = \begin{pmatrix} . & . & . & . \\ . & 1 & . & . \\ . & . & . & . \\ . & . & . & 1 \end{pmatrix} \quad (4-6)$$

$E$  is the  $4 \times 4$  unit matrix and  $O$  the  $4 \times 4$  nul matrix.

The non-zero characters are

$$\begin{aligned} \chi(e) &= 8; \chi(2_x) = \chi(\bar{1}) = \chi(2_x \bar{1}) = \chi(4_1^2 2_x) = \\ &\chi(t \bar{1}) = \chi(t 4_1^2 2_x \bar{1}) = 4 \end{aligned} \quad (4-7)$$

and the reduction of  $\Gamma^{\text{perm}}$  yields

$$\Gamma^{\text{perm}}(\text{Cr}) = \Gamma_{1g}(\mathbf{k}_1) + \Gamma_{3g}(\mathbf{k}_1) + \Gamma_{5g}(\mathbf{k}_1) + \Gamma_1^+(\mathbf{k}_2) + \Gamma_2^+(\mathbf{k}_2). \quad (4-8)$$

According to (4-4) and (4-8) the dimensions of the present irreducible representations are equally distributed over the wave vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$ , *i.e.* over lattice translations and anti-translations.

## 5. Representation of magnetic modes

A space group operation  $T = \{\alpha | \tau_\alpha\}$  acting on a magnetic moment, say on an axial vector at point  $R$  may be decomposed into two independent and commuting operations. A first operation sends point  $R$  to another one  $R'$  giving rise to the already discussed permutation representation. A second operation  $\alpha$  rotates the axial vector about a fixed point. Thus the representation  $\Gamma$  induced by the operation of space group elements on magnetic moments is the direct product of the permutation representation  $\Gamma^{\text{perm}}$  and the representation  $\Gamma^V$  of the  $x, y, z$  components of an axial vector,

$$\Gamma = \Gamma^{\text{perm}} \times \Gamma^V. \quad (5-1)$$

The same direct product relation holds for the matrix representatives of a space group operation  $T$ . The corresponding relation for characters is simply

$$\chi^T(T) = \chi^{\text{perm}}(T) \chi^V(T). \quad (5-2)$$

In uniaxial crystals  $\Gamma^V$  splits into a one-dimensional representation  $\Gamma_z^V$  for the  $z$  component and a two-dimensional representation  $\Gamma_{x,y}^V$  for the  $x, y$  components. In the present case  $\Gamma_z^V$  is clearly  $\Gamma_{2g}(\mathbf{k}_1)$  and  $\Gamma_{x,y}^V$  is  $\Gamma_{5g}(\mathbf{k}_1)$  so that  $\Gamma$  splits already into subspace representations

$$\Gamma = \Gamma_{x,y} + \Gamma_z \quad (5-3)$$

with

$$\Gamma_z = \Gamma^{\text{perm}} \times \Gamma_{2g}(\mathbf{k}_1); \Gamma_{x,y} = \Gamma^{\text{perm}} \times \Gamma_{5g}(\mathbf{k}_1). \quad (5-4)$$

Thus we get for the  $z$  components of magnetic moments

$$\begin{aligned}\Gamma_z(\text{Ni}) &= \Gamma_{2g} + \Gamma_{3u} + \Gamma_1^- \\ \Gamma_z(\text{Cr}) &= \Gamma_{2g} + \Gamma_{4g} + \Gamma_{5g} + \Gamma_1^- + \Gamma_2^- \end{aligned} \quad (5-5)$$

and for the  $x, y$  components

$$\begin{aligned}\Gamma_{x,y}(\text{Ni}) &= \Gamma_{5g} + \Gamma_{5u} + \Gamma_2^+ + \Gamma_2^- \\ \Gamma_{x,y}(\text{Cr}) &= \Gamma_{1g} + \Gamma_{2g} + \Gamma_{3g} + \Gamma_{4g} + 2\Gamma_{5g} + \Gamma_1^+ + \Gamma_1^- + \Gamma_2^+ + \Gamma_2^- \end{aligned} \quad (5-6)$$

$$\begin{aligned}T: & \mathbf{1} \quad \mathbf{4}_1 \quad \mathbf{4}_1^2 \quad \mathbf{4}_1^3 \quad \mathbf{2}_x \quad \mathbf{4}_1\mathbf{2}_x \quad \mathbf{4}_1^2\mathbf{2}_x \quad \mathbf{4}_1^3\mathbf{2}_x \text{ etc.} \\ T\psi: & \mathcal{S}_{1x} \cdot -\mathcal{S}_{2y} \cdot -\mathcal{S}_{3x} \cdot +\mathcal{S}_{4y} \cdot \mathcal{S}_{2x} \cdot -\mathcal{S}_{3y} \cdot -\mathcal{S}_{4x} \cdot +\mathcal{S}_{1y} \end{aligned} \quad (6-2)$$

In the last relations we have used

$$\begin{aligned}\Gamma_1^+(\mathbf{k}_2) \times \Gamma_{5g}(\mathbf{k}_1) &= \Gamma_2^+(\mathbf{k}_2) + \Gamma_2^-(\mathbf{k}_2) \\ \Gamma_2^+(\mathbf{k}_2) \times \Gamma_{5g}(\mathbf{k}_1) &= \Gamma_1^+(\mathbf{k}_2) + \Gamma_1^-(\mathbf{k}_2) \end{aligned} \quad (5-7)$$

We are now in a position to survey the distribution of permitted magnetic modes over the different representations. This is done in Table 3. For the  $\mathbf{k}_1$  modes it is seen that coupling of the magnetic lattices of Ni and Cr is only possible in  $\Gamma_{2g}$  and in  $\Gamma_{5g}$ . One of these modes is expected to give rise to the observed ferrimagnetism. In the  $\mathbf{k}_2$ -modes coupling of Ni and Cr modes is possible in  $\Gamma_1^-$ ,  $\Gamma_2^+$  and  $\Gamma_2^-$ .

Table 3. Irreducible representations and couplings

Representations $\Gamma(k_1)$	Positions 4(a)		Positions 8(d)	
	$x, y$	$z$	$x, y$	$z$
$\Gamma_{1g}$	—	—	Cr	—
$\Gamma_{2g}$	—	Ni	Cr	Cr
$\Gamma_{3g}$	—	—	Cr	—
$\Gamma_{4g}$	—	—	Cr	Cr
$\Gamma_{5u}$	Ni	—	Cr	Cr
$\Gamma_{3g}$	—	Ni	—	—
$\Gamma_{5u}$	Ni	—	—	—
Representations $\Gamma(k_2)$				
$\Gamma_1^+$	—	—	Cr	—
$\Gamma_1^-$	—	Ni	Cr	Cr
$\Gamma_2^+$	Ni	—	Cr	—
$\Gamma_2^-$	Ni	—	Cr	Cr

## 6. Magnetic modes

We use the so called projection operator technique: let  $\psi$  be a component or a linear combination of components of a magnetic moment or spin. In most cases it is sufficient to take  $\psi = \mathcal{S}_{1\alpha}$  with  $\alpha = x, y, z$ . Let  $T\psi$  be the result of the action of the space group element  $T$  on  $\psi$  and multiply  $T\psi$  by  $D^{(\nu)}(T)^*_{ij}$ , element of the matrix  $D^{(\nu)}(T)^*$  representative of  $T$  in the irreducible representation  $\Gamma^{(\nu)}$ . The asterisk indicates complex conjugation. The sum over group elements  $T$  of such products is noted

$$\psi_{ij}^{(\nu)} = \sum_T D^{(\nu)}(T)^*_{ij} T\psi. \quad (6-1)$$

It can be shown that  $\psi_{ij}^{(\nu)}$  with  $j$  fixed and  $i = 1, 2, \dots, d_\nu$  ( $d_\nu$  = dimension of the irreducible representation  $\Gamma^{(\nu)}$ ) transforms according to the representation  $\Gamma^{(\nu)}$  or is a basis vector of  $\Gamma^{(\nu)}$ .

The following part of a table illustrates in the first line the symmetry operations  $T$  and in the second line the effect, say  $T\psi$  in the case of Ni with  $\psi = \mathcal{S}_{1x}$

For the  $\mathbf{k}_1$ -modes one has  $\mathcal{S}_1 = \mathcal{S}_3$  and  $\mathcal{S}_2 = \mathcal{S}_4$  while for the  $\mathbf{k}_2$ -modes one has  $\mathcal{S}_1 = -\mathcal{S}_3$ ;  $\mathcal{S}_2 = -\mathcal{S}_4$ .

With the help of relations (6-1) and Tables 1 and 2 it is easy to construct the basis vectors. The only non-zero basis vectors belong to the representations of relations (5-5) and (5-6).

### Ni $\mathbf{k}_1$ modes

$$\begin{aligned}\psi^{(2g)} &= (\mathcal{S}_1 + \mathcal{S}_2)_z; \quad \psi^{(3u)} = (\mathcal{S}_1 - \mathcal{S}_2)_z; \\ \psi_{11}^{(5g)} &= (\mathcal{S}_1 + \mathcal{S}_2)_x + i(\mathcal{S}_1 + \mathcal{S}_2)_y, \quad \psi_{21}^{(5g)} = \psi_{11}^{(5g)}; \\ \psi_{11}^{(5u)} &= (\mathcal{S}_1 - \mathcal{S}_2)_x + i(\mathcal{S}_1 - \mathcal{S}_2)_y, \quad \psi_{21}^{(5u)} = \psi_{11}^{(5u)}. \end{aligned} \quad (6-3)$$

### Ni $\mathbf{k}_2$ modes

$$\begin{aligned}\psi_{11}(\Gamma_1^-) &= (\mathcal{S}_1 - i\mathcal{S}_2)_z, \quad \psi_{21} = i\psi_{11}^*; \\ \psi_{11}(\Gamma_2^+) &= (\mathcal{S}_1 + \mathcal{S}_2)_x + (\mathcal{S}_1 - \mathcal{S}_2)_y, \\ \psi_{21}(\Gamma_2^+) &= (\mathcal{S}_1 + \mathcal{S}_2)_x - (\mathcal{S}_1 - \mathcal{S}_2)_y; \\ \psi_{11}(\Gamma_2^-) &= (\mathcal{S}_1 - \mathcal{S}_2)_x - (\mathcal{S}_1 + \mathcal{S}_2)_y, \\ \psi_{21}(\Gamma_2^-) &= -(\mathcal{S}_1 - \mathcal{S}_2)_x - (\mathcal{S}_1 + \mathcal{S}_2)_y. \end{aligned} \quad (6-4)$$

These relations can be illustrated by graphs or 'modes'. As an example let us assume that a magnetic structure belongs to  $\Gamma_2^-$ . This means that basis vectors belonging to other representations, say to  $\Gamma_2^+$  disappear identically whence  $\mathcal{S}_{1x} = -\mathcal{S}_{2x}$  and  $\mathcal{S}_{1y} = +\mathcal{S}_{2y}$ . If we make  $\mathcal{S}_{1x} = -\mathcal{S}_{1y}$ ,  $\psi_{11}(\Gamma_2^-)$  is maximum with  $\psi_{21} = 0$ . If we make  $\mathcal{S}_{1x} = +\mathcal{S}_{1y}$ ,  $\psi_{21}(\Gamma_2^-)$  is maximum with  $\psi_{11} = 0$ . Fig. 1 illustrates these findings.

One proceeds as above for the Cr modes

### Cr $\mathbf{k}_1$ modes

$$\begin{aligned}\psi_x^{(1g)} &= \mathcal{S}_{1x} - \mathcal{S}_{2y} - \mathcal{S}_{3x} + \mathcal{S}_{4y}; \\ \psi_y^{(2g)} &= \mathcal{S}_{1y} + \mathcal{S}_{2x} - \mathcal{S}_{3y} - \mathcal{S}_{4x}, \quad \psi_z^{(2g)} = (\mathcal{S}_1 + \mathcal{S}_2 + \mathcal{S}_3 + \mathcal{S}_4)_z; \\ \psi_x^{(3g)} &= \mathcal{S}_{1x} + \mathcal{S}_{2y} - \mathcal{S}_{3x} - \mathcal{S}_{4y}; \\ \psi_y^{(4g)} &= \mathcal{S}_{1y} - \mathcal{S}_{2x} - \mathcal{S}_{3y} + \mathcal{S}_{4x}, \quad \psi_z^{(4g)} = (\mathcal{S}_1 - \mathcal{S}_2 + \mathcal{S}_3 - \mathcal{S}_4)_z; \\ \psi_{11x}^{(5g)} &= (\mathcal{S}_1 + \mathcal{S}_3)_x + i(\mathcal{S}_2 + \mathcal{S}_4)_y, \quad \psi_{21x}^{(5g)} = \psi_{11x}^{(5g)}; \\ \psi_{11y}^{(5g)} &= (\mathcal{S}_1 + \mathcal{S}_3)_y - i(\mathcal{S}_2 + \mathcal{S}_4)_x, \quad \psi_{21y}^{(5g)} = \psi_{11y}^{(5g)*}; \\ \psi_{11z}^{(5g)} &= (\mathcal{S}_1 - \mathcal{S}_3)_z - i(\mathcal{S}_2 - \mathcal{S}_4)_z, \quad \psi_{21z}^{(5g)} = \psi_{11z}^{(5g)*}. \end{aligned} \quad (6-5)$$

### Cr $\mathbf{k}_2$ modes

$$\begin{aligned}\psi_{11}(\Gamma_1^+) &= (\mathcal{S}_1 + \mathcal{S}_3)_x + i(\mathcal{S}_2 + \mathcal{S}_4)_y, \quad \psi_{21} = \psi_{11}^*; \\ \psi_{11y}(\Gamma_1^-) &= (\mathcal{S}_1 + \mathcal{S}_3)_y - i(\mathcal{S}_2 + \mathcal{S}_4)_x, \quad \psi_{21y} = -\psi_{11y}^*; \\ \psi_{11z}(\Gamma_1^-) &= (\mathcal{S}_1 - \mathcal{S}_3)_z - i(\mathcal{S}_2 - \mathcal{S}_4)_z, \quad \psi_{21z} = -\psi_{11z}^*; \end{aligned}$$

$$\begin{aligned}
\psi_{11x}(\Gamma_2^+) &= (\mathcal{S}_1 - \mathcal{S}_3)_x - (\mathcal{S}_2 - \mathcal{S}_4)_y, \\
\psi_{21x}(\Gamma_2^+) &= (\mathcal{S}_1 - \mathcal{S}_3)_x + (\mathcal{S}_2 - \mathcal{S}_4)_y; \\
\psi_{11y}(\Gamma_2^-) &= (\mathcal{S}_1 - \mathcal{S}_3)_y + (\mathcal{S}_2 - \mathcal{S}_4)_x, \\
\psi_{21y}(\Gamma_2^-) &= (\mathcal{S}_1 - \mathcal{S}_3)_y - (\mathcal{S}_2 - \mathcal{S}_4)_x; \\
\psi_{11z}(\Gamma_2^-) &= (\mathcal{S}_1 + \mathcal{S}_3)_z + (\mathcal{S}_2 + \mathcal{S}_4)_z, \\
\psi_{21z}(\Gamma_2^-) &= (\mathcal{S}_1 + \mathcal{S}_3)_z - (\mathcal{S}_2 + \mathcal{S}_4)_z.
\end{aligned} \quad (6-6)$$

We have not listed the basis vectors ( $\psi_{12}$ ,  $\psi_{22}$ ) because they are (except for changes of sign) identical with the basis vectors ( $\psi_{11}$ ,  $\psi_{21}$ ).

For practical purposes it is useful to write the relations (6-3) to (6-6) in Table 3 on the lines to which they belong.

It can be checked that the number of basis vectors is identical to  $3n$ , if  $n$  is the number of equivalent points.

### 7. Intensity calculations

In straightforward notation, the magnetic structure factor is defined by the vector sum

$$\mathbf{F}(\mathbf{h}) = \sum \mathcal{S}_j f_j(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j). \quad (7-1)$$

The magnetic intensity is given by

$$I(\mathbf{h}) = |\mathbf{F}(\mathbf{h})|^2 - |\mathbf{F}(\mathbf{h}) \cdot \mathbf{h}|^2 / |\mathbf{h}|^2 \quad (7-2)$$

#### 7.1. Antiferromagnetic lines

From the calculations of  $\mathbf{F}(\mathbf{h})$  one sees that the magnetic moments of chromium only occur in the combinations  $\mathcal{S}_1 + \mathcal{S}_3$ ,  $\mathcal{S}_2 + \mathcal{S}_4$ ,  $\mathcal{S}_1 - \mathcal{S}_3$  and  $\mathcal{S}_2 - \mathcal{S}_4$ . We have found it convenient to define vectors  $\mathbf{S}_j$  and  $\mathbf{s}_j$  for the Cr moments as follows

$$\begin{aligned}
\mathcal{S}_1 &= \mathbf{S}_1 + \mathbf{s}_1; \quad \mathcal{S}_2 = \mathbf{S}_2 + \mathbf{s}_2 \\
\mathcal{S}_3 &= \mathbf{S}_1 - \mathbf{s}_1; \quad \mathcal{S}_4 = \mathbf{S}_2 - \mathbf{s}_2.
\end{aligned} \quad (7-3)$$

In a powder diagram, reflexions for which  $|\mathbf{h}|$  has the same length coincide. The averaged intensities are noted  $\langle I\{\mathbf{h}\} \rangle$ . Thus  $\langle I\{111\} \rangle$  means the average of the intensities of the eight reflexions 111,  $\bar{1}\bar{1}\bar{1}$ ,  $1\bar{1}\bar{1}$ ,  $1\bar{1}\bar{1}$ ,  $\bar{1}\bar{1}1$ ,  $\bar{1}\bar{1}1$ ,  $1\bar{1}1$ ,  $\bar{1}\bar{1}1$ . The evaluation of  $\langle I\{\mathbf{h}\} \rangle$  is tedious, but straightforward. The result may be written as follows

$$\langle I\{\mathbf{h}\} \rangle = \langle I_0\{\mathbf{h}\} \rangle + \text{Interference term.} \quad (7-4)$$

Here

$$\langle I_0\{\mathbf{h}\} \rangle = \langle I_{\text{Cr}}\{\mathbf{h}\} \rangle + \langle I_{\text{Ni}}\{\mathbf{h}\} \rangle \quad (7-5)$$

where  $\langle I_{\text{Cr}} \rangle$  and  $\langle I_{\text{Ni}} \rangle$  are the averaged intensities for the separate sublattices of Cr and Ni respectively, calculated according to (7-2). For completeness these intensities are summarized in the Appendix. One has for the antiferromagnetic reflexions

$$\begin{aligned}
\langle I\{111\} \rangle &= \langle I_0\{111\} \rangle - 8\sqrt{2}d_{111}^2 A \\
\langle I\{102\} \rangle &= \langle I_0\{102\} \rangle + 16d_{102}^2 A
\end{aligned} \quad (7-6)$$

with the abbreviations

$$\begin{aligned}
A &= b_1 b_3 [(\mathcal{S}_1 + \mathcal{S}_2)_{z\text{Ni}} S_{1y\text{Cr}} - (\mathcal{S}_1 - \mathcal{S}_2)_{z\text{Ni}} S_{2x\text{Cr}} \\
&\quad + (\mathcal{S}_1 + \mathcal{S}_2)_{y\text{Ni}} S_{3z\text{Cr}} - (\mathcal{S}_1 - \mathcal{S}_2)_{x\text{Ni}} S_{2z\text{Cr}}] \\
b &= a^{-1}; \quad b_3 = c^{-1}
\end{aligned} \quad (7-7)$$

and also

$$\begin{aligned}
\langle I\{100\} \rangle &= \langle I_0\{100\} \rangle + 8(B_x + B_z) \\
\langle I\{001\} \rangle &= \langle I_0\{001\} \rangle - 8\sqrt{2}(B_x + B_y) \\
\langle I\{201\} \rangle &= \langle I_0\{201\} \rangle + 16\sqrt{2}(-B_y + B_x).
\end{aligned} \quad (7-8)$$

Here we have abbreviated

$$B_\alpha = s_{1\alpha\text{Cr}}(\mathcal{S}_1 + \mathcal{S}_2)_{\alpha\text{Ni}} - s_{2\beta\text{Cr}}(\mathcal{S}_1 - \mathcal{S}_2)_{\beta\text{Ni}} \quad (7-9)$$

with the following conventions: if  $\alpha = x$ ,  $\beta = y$ ; if  $\alpha = y$ ,  $\beta = x$  and if  $\alpha = z$ ,  $\beta = z$ .

#### Discussion of intensities

Some remarkable facts for the magnetic structure under discussion emerge here already. The interference term noted  $A$  (7-7) occurs with opposite sign in the intensities of 111 and 102 and thus is expected to strengthen the 111 reflexion which is observed strong and to weaken the 102 reflexion which is observed weak. The existence of a non-zero term  $A$  implies anisotropic exchange between the Cr and Ni atoms, for it links  $z$  components to  $x$  and (or)  $y$  components of moments. Another consequence is the impossibility of ferrimagnetism along  $Oz$ . Indeed ferrimagnetism along  $Oz$  would not be compatible with antiferromagnetism along the same axis, for equivalent atoms must have equal moments. On the other hand it is seen that if there is no antiferromagnetic component along  $Oz$  the interference term  $A$  disappears. Thus antiferromagnetism along  $Oz$  in one sublattice and in the  $Oxy$  plane in the other sublattice appears to be necessary.

In the expression for the intensities 100, 001 and 201, interference terms, labelled  $B$  and corresponding to isotropic interactions, appear in such a way that 001 and 201 should become negligible.

However a discussion of possible antiferromagnetic modes, guided only by the intensity expressions, would be rather hopeless in view of the great number of parameters involved.

#### 7.2. Ferrimagnetic lines

From the structure factor calculations of the reflexions 110,  $1\bar{1}0$  and 002 which are not observed and from the above mentioned impossibility of ferrimagnetism along  $Oz$ , one must draw the following conclusions for the ferrimagnetic components (denoted by the subscript  $f$ )

$$\begin{aligned}
\mathcal{S}_{1f\text{Ni}} &= \mathcal{S}_{2f\text{Ni}}; \quad \mathcal{S}_{1f\text{Cr}} = \mathcal{S}_{3f\text{Cr}}; \quad \mathcal{S}_{2f\text{Cr}} = \mathcal{S}_{4f\text{Cr}}; \\
\mathcal{S}_{1f\text{Cr}} &\simeq \mathcal{S}_{2f\text{Cr}}, \quad (7-10)
\end{aligned}$$

i.e. an equal contribution of all the chromium moments to the ferrimagnetic mode.

### 8. Model construction

Ferrimagnetism in the  $Oxy$  plane can be realized in  $\Gamma_{5g}$ .

### 8.1. Ferrimagnetism along $Ox$

Let us assume a ferrimagnetism along  $Ox$ , say

$$\begin{aligned} S_{1xf}(\text{Ni}) &= S_{2xf}(\text{Ni}); S_{1xf}(\text{Cr}) = S_{3xf}(\text{Cr}); \\ S_{2xf}(\text{Cr}) &= S_{4xf}(\text{Cr}) \end{aligned} \quad (8-1)$$

which gives rise to non-zero basis vectors in  $\Gamma_{5g}$ .

Components of the same spin but belonging to different representations must be orthogonal. Thus for the construction of the antiferromagnetic moments we are only allowed to take  $y$  and  $z$  components. The representation which from the point of view of the physicist is the most probable is the representation offering the greatest number of possible couplings. This is  $\Gamma_{2^-}$ . We read then from the basis vectors in (6-4) and (6-6) that we shall have the following model to deal with

$$\begin{aligned} \mathcal{S}_{1y}(\text{Ni}) &= \mathcal{S}_{2y}(\text{Ni}); s_{1y}(\text{Cr}) = -s_{3y}(\text{Cr}); \\ S_{2z}(\text{Cr}) &= +S_{4z}(\text{Cr}); S_{1z}(\text{Cr}) = +S_{3z}(\text{Cr}). \end{aligned} \quad (8-2)$$

which gives rise to the following intensities

$$\begin{aligned} \langle I(111) \rangle &= 8[t^2 + 2u^2 - d_{111}^2(bt + \sqrt{2}b_3u)^2 \\ &\quad + 2w^2(1 - d_{111}^2b_3^2)] \\ \langle I(102) \rangle &= 8[u^2 + v^2 + t^2 - d_{102}^2(bt - 2b_3u)^2 \\ &\quad + w^2(1 - 4d_{102}^2b_3^2)] \\ \langle I(001) \rangle &= 8(t - \sqrt{2}v)^2 \\ \langle I(100) \rangle &= 8[(t + v)^2 + u^2 + w^2] \\ \langle I(201) \rangle &= 8[t^2 + 2v^2 - 2d_{201}^2b^2(t + \sqrt{2}v)^2]. \end{aligned} \quad (8-3)$$

Here we have abbreviated

$$\begin{aligned} \mathcal{S}_{1y}(\text{Ni})f_{\text{Ni}}(h) &= t; s_{1y}(\text{Cr})f_{\text{Cr}}(h) = v; \\ S_{1z}(\text{Cr})f_{\text{Cr}}(h) &= u; S_{2z}(\text{Cr})f_{\text{Cr}}(h) = w. \end{aligned} \quad (8-4)$$

Of course  $t, u, v, w$  in (8-3) are functions of the diffusion vector  $\mathbf{h}$ . The above equations (8-3) already provide a qualitative picture of the observed intensities. Indeed, if  $t$  and  $u$  have opposite signs,  $I(111)$  will be strengthened and  $I(102)$  weakened. If  $t$  and  $v$  have the same sign,  $I(001)$  can be made to disappear,  $I(201)$  will be weakened and  $I(100)$  strengthened as is observed.

### 8.2 Ferrimagnetism along $Oy$

It can be easily checked that one has in  $\Gamma_{5g}$

$$\begin{aligned} S_{1yf}(\text{Ni}) &= S_{2yf}(\text{Ni}); S_{1yf}(\text{Cr}) = S_{3yf}(\text{Cr}); \\ S_{2yf}(\text{Cr}) &= S_{4yf}(\text{Cr}) \end{aligned} \quad (8-5)$$

and in  $\Gamma_{2^-}$

$$\begin{aligned} \mathcal{S}_{1x}(\text{Ni}) &= -\mathcal{S}_{2x}(\text{Ni}); s_{2x}(\text{Cr}) = -s_{4x}(\text{Cr}) \\ S_{2z}(\text{Cr}) &= S_{4z}(\text{Cr}); S_{1z}(\text{Cr}) = S_{3z}(\text{Cr}). \end{aligned} \quad (8-6)$$

It is seen that in this model the role of the chromium moments 1 and 3 is taken over by those of 2 and 4 and *vice versa*. The two models as shown in Fig. 2 behave

like twins and give rise to the same intensities. For completeness we show this by direct calculation. With the abbreviations

$$\begin{aligned} \mathcal{S}_{1x}(\text{Ni})f_{\text{Ni}}(h) &= t'; s_{2x}(\text{Cr})f_{\text{Cr}}(h) = -v' \\ S_{2z}(\text{Cr})f_{\text{Cr}}(h) &= -u'; S_{1z}(\text{Cr})f_{\text{Cr}}(h) = w' \end{aligned} \quad (8-7)$$

one finds exactly the same equations (8-3), primed letters having replaced the unprimed ones.

To see the twin relation between the upper and lower parts of Fig. 2, rotate the upper part around the fourfold screw axis marked by a cross and change the signs of all the spin components. One obtains exactly the lower part of Fig. 2. It is remarkable that the  $z$  components do not change in either model.

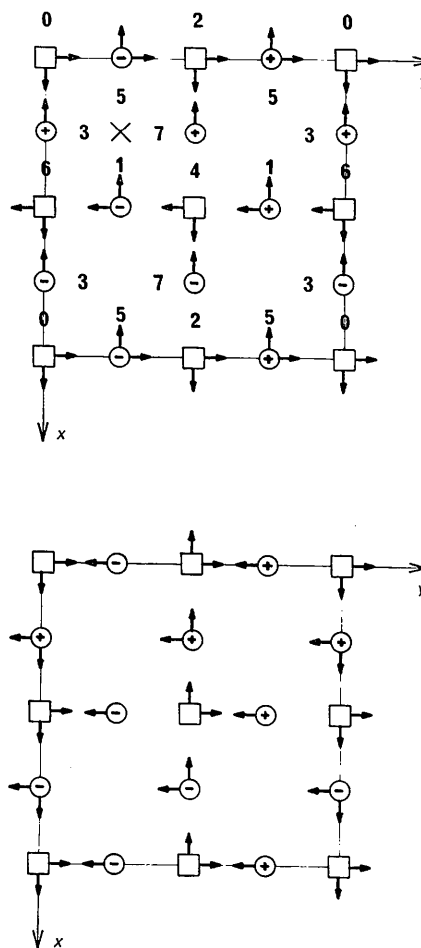


Fig. 2. Structure models. Upper part: Ferrimagnetism along  $Ox$ . Tetrahedral sites are marked by squares, octahedral sites by circles. Heights are indicated in eighths of the  $c$  parameter: 0, 2, 4, 6 for the tetrahedral, 1, 3, 5, 7 for the octahedral sites. Thus the numbering of chromium atoms 1, 2, 3, 4 of the text corresponds to the heights 5, 7, 1, 3 respectively around the cross  $\times$  which shows the location of the fourfold clock-wise crystallographic screw axis. Spin directions in the  $Oxy$  plane are indicated by arrows and in the  $Oz$  direction by  $+$  and  $-$  signs. Lower part: Ferrimagnetism along  $Oy$ : Same conventions as above.

### 8.3. Spin components

We used a multiplicative scaling factor of 3.699 to bring the data taken by Prince (1961, Table I) at 77 and 4.2°K to an absolute scale. From the reflexions 112+200 and 101 we deduce the ferrimagnetic spin components

$$S_{x,f}(\text{Ni})=0.82; S_{x,f}(\text{Cr}_1)=S_{x,f}(\text{Cr}_2)=0.70 \quad (8-8)$$

and from the antiferromagnetic reflexions

$$\begin{aligned} \mathcal{S}_y(\text{Ni}) &= 0.58; S_z(\text{Cr}_1) = -0.45; \\ s_y(\text{Cr}_1) &= +0.73; S_z(\text{Cr}_2) = 0.86. \end{aligned} \quad (8-9)$$

In the evaluation we have supposed that  $I(001)$  is strictly zero [ $t(001)=\sqrt{2} \cdot v(001)$ ]; that  $I(111)$  is maximal [ $u(111)=-c/a\sqrt{2}t(111)$ ] and that the two chromium species have the same total spin values. The total spins are thus  $\mathcal{S}_{\text{tot}}(\text{Ni})=1.0$  and  $\mathcal{S}_{\text{tot}}(\text{Cr})=1.11$  and the moment values  $\mu(\text{Ni})=2.0\mu_\beta \pm 0.2\mu_\beta$  and  $\mu(\text{Cr})=2.22\mu_\beta \pm 0.2\mu_\beta$ .

### 9. Shubnikov symmetry

It is easy to read from Fig. 2 those symmetry elements which leave the magnetic structure invariant.

Consider first the ferrimagnetic component along  $Ox$  which is invariant under the translation  $\mathbf{t}$ , the inversion  $I$ , a twofold axis  $2_x$  and antiaxes  $2'_y$  in  $\frac{1}{2}, y, \frac{3}{4}$  and  $2'_z$  in  $\frac{1}{2}, \frac{1}{2}, z$ . The Shubnikov group would be  $Imm'a'$ .

The antiferromagnetic component is invariant under an antitranslation  $\mathbf{t}'$ , under the screw axis  $2_{1z}$  in  $\frac{1}{2}\frac{1}{2}z$  and under the anti-axes  $2'_x$  and  $2'_y$ . The inversion centre is lost and the Shubnikov group would be  $I_p2'2'_1$ .

The overall symmetry is the intersection of  $Imm'a'$  and  $I_p2'2'_1$  so that we are left with  $P2'_y$ . Considering in the same way the case of ferrimagnetism along  $Oy$  we arrive at the equivalent symmetry  $P2'_x$ . We doubt that a conventional symmetry descent through Shubnikov groups would have given rise to the rather straightforward derivation of the magnetic structure as did the present representation analysis.

### 10. Invariants and magnetic interactions

One of the essential advantages of representation analysis is the possibility of getting insight into magnetic interactions. Indeed from the knowledge of basis vectors, one constructs invariants which may enter a 'classical spin Hamiltonian'. Such invariants are in the case of two-dimensional representations  $|\psi_{11}|^2 + |\psi_{21}|^2$  for interactions between the same kind of atoms and  $(\psi_{11})(\psi'_{11})^* + (\psi_{21})(\psi'_{21})^* + \text{c.c.q.}$  for interactions between different species or different directions.

Considering the interactions in the antiferromagnetic  $\Gamma^-(\mathbf{k}_2)$ -modes, the ferrimagnetism being along  $Ox$ , one finds the following invariants and interactions:

**Ni sublattice.** —  $\mathcal{S}_{1y}\mathcal{S}_{2y}$ , positive interaction through super-super exchange;

**Cr sublattice.** — (a) —  $\mathcal{S}_{1y}\mathcal{S}_{3y}=\mathcal{S}_{1y}\mathcal{S}_{7y}$ . Here we have replaced  $\mathcal{S}_{3y}$  by the equivalent antitranslated spin  $\mathcal{S}_{7y}$  with Cr(7) in  $0\frac{3}{4}\frac{5}{8}$  which is the nearest neighbour of Cr(1) in  $0\frac{1}{4}\frac{5}{8}$ . The interaction corresponds to positive exchange along  $Oy$ .

(b)  $\mathcal{S}_{1z}\mathcal{S}_{3z}+\mathcal{S}_{2z}\mathcal{S}_{4z}=-\mathcal{S}_{1z}\mathcal{S}_{7z}-\mathcal{S}_{2z}\mathcal{S}_{8z}$ . This corresponds to negative exchange along  $Oz$ .

**Remark.** — In the right-angle interaction  $\text{Cr}^{3+}-\text{X}-\text{Cr}^{3+}$ , negative direct exchange interactions Cr-Cr are competing with positive super-exchange interactions through the anion X. The resulting interaction is negative for small Cr-Cr distances (small anion X, O for instance) and positive for big ones (Te for instance). In the present case one has for the same magnetic link Cr-X-Cr a positive interaction along  $Oy$  and a negative interaction along  $Oz$  so that here interactions are strongly direction dependent.

(c) —  $(\mathcal{S}_{1y}\mathcal{S}_{1z}-\mathcal{S}_{3y}\mathcal{S}_{3z})+(\mathcal{S}_{1y}\mathcal{S}_{3z}-\mathcal{S}_{1z}\mathcal{S}_{3y})$ . This invariant splits into a crystal field — or 'one ion anisotropy' — invariant and an antisymmetric exchange (Dzialoshinski-Moriya) invariant. Both of them may justify the non colinear  $y$ - $z$  coupling.

### Ni-Cr interactions

—  $\mathcal{S}_{1y\text{Ni}}\mathcal{S}_{1y\text{Cr}}$  isotropic negative exchange

—  $\mathcal{S}_{1y\text{Ni}}\mathcal{S}_{1z\text{Cr}}$  anisotropic exchange

Our symmetry considerations show the possibilities of coupling. The next step should be a quantum mechanical treatment, evaluating the strength of possible couplings.

A more complete experimental analysis using variable temperatures and applied magnetic fields is in progress.

## APPENDIX

### Sublattice intensities

Cr

$$\langle I_{\text{Cr}}\{111\} \rangle = 16 \sum \{ S^2 - d_{111}^2 [b^2(S_x^2 + S_y^2) + b_3^2 S_z^2] \}$$

$$\begin{aligned} \langle I_{\text{Cr}}\{102\} \rangle &= 8 \{ \sum (S^2 + s^2) - d_{102}^2 [b^2(S_{1y}^2 + S_{2x}^2 + s_{1x}^2 + s_{2y}^2) \\ &\quad + 4b_3^2 \sum (S_z^2 + s_z^2)] \} \end{aligned}$$

$$\langle I_{\text{Cr}}\{100\} \rangle = 8 \{ S_{1x}^2 + S_{2y}^2 + s_{1y}^2 + s_{2x}^2 + \sum (S_z^2 + s_z^2) \}$$

$$\langle I_{\text{Cr}}\{201\} \rangle = 16 \sum \{ s^2 - d_{201}^2 [2b^2(s_x^2 + s_y^2) + b_3^2 s_z^2] \}$$

$$\langle I_{\text{Cr}}\{001\} \rangle = 16 \{ \sum (s_x^2 + s_y^2) \}$$

$\sum$  = summation over  $\text{Cr}_1$  and  $\text{Cr}_2$ .

Ni

$$\langle I_{\text{Ni}}\{111\} \rangle = 4 \sum \{ \mathcal{S}_{\text{Ni}}^2 - d_{111}^2 [b^2(\mathcal{S}_x^2 + \mathcal{S}_y^2)_{\text{Ni}} + b_3^2 \mathcal{S}_z^2] \}$$

$$\begin{aligned} \langle I_{\text{Ni}}\{102\} \rangle &= 4 \sum \{ \mathcal{S}_{\text{Ni}}^2 - d_{102}^2 [2b^2 \sum (\mathcal{S}_x^2 + \mathcal{S}_y^2) \\ &\quad + 2(\mathcal{S}_{1y}\mathcal{S}_{2y} - \mathcal{S}_{1x}\mathcal{S}_{2x})] + 16b_3^2 \sum \mathcal{S}_z^2 \} \end{aligned}$$

$$\begin{aligned} \langle I_{\text{Ni}}\{100\} \rangle &= 2 \{ \sum (\mathcal{S}_x^2 + \mathcal{S}_y^2) + 2(\mathcal{S}_{1y}\mathcal{S}_{2y} - \mathcal{S}_{1x}\mathcal{S}_{2x}) \} \\ &\quad + 4 \sum \mathcal{S}_z^2 \end{aligned}$$



$$\langle I_{\text{Ni}}\{201\} \rangle = 4 \sum \{ \mathcal{S}_{\text{Ni}}^2 - d_{201}^2 [2b^2(\mathcal{S}_x^2 + \mathcal{S}_y^2) + b_3^2 \mathcal{S}_z^2] \}$$

$$\langle I_{\text{Ni}}\{001\} \rangle = 4 \sum (\mathcal{S}_x^2 + \mathcal{S}_y^2)$$

$\Sigma$  = summation over Ni<sub>1</sub> and Ni<sub>2</sub>.

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## The Dynamical Scattering Amplitude of an Imperfect Crystal. II. A Relation Between Takagi's Dynamical Equation and a More Exact Dynamical Equation

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A basic equation of dynamical diffraction for an imperfect crystal is derived based on a general dynamical theory of diffraction. This equation is given in the form of a differential equation, and therefore can be considered to describe the diffraction processes locally inside a crystal. A phenomenological interpretation of this equation helps to fill in the gap between modern quantum mechanical treatments and ordinary treatments by dynamical theory of diffraction for a perfect crystal. In the approximation of poor resolution the more exact equation reduces to Takagi's equation. A necessary condition which makes Takagi's equation valid leads to the concept of local reciprocal lattice vectors.

### 1. Introduction

A general dynamical theory of diffraction for an imperfect crystal has been formulated previously by use of a quantum field theoretical technique\* (Ashkin & Kuriyama, 1966; Kuriyama, 1967*a,b*, 1968). The validity of this theory is not restricted by the magnitudes of strains (atomic displacements), and types of imperfections, nor by the state of the incident beam. This theory is constructed from an atomistic point of view: the generalized polarizability for X-rays or the generalized crystal potential for incoming electrons does not possess periodic translational invariance in imperfect crystals.

Much of the physics involved in diffraction from imperfect crystals has been discussed in a previous paper (Kuriyama, 1969) where a standard iteration technique is applied to this new formulation; the effects of crystal imperfections on dynamical diffraction have been treated correctly by properly accounting for the phase modulation of the diffracted beams, and not as a result of the assumption of modified Bloch waves.

Using this new formulation, a dynamical expression for the scattering amplitude of an imperfect crystal has been derived in a compact form (Kuriyama, 1970; hereafter this paper will be referred to as I).

On the other hand there have appeared a number of works on the dynamical theory of diffraction in imperfect crystals (Penning & Polder, 1961, 1964; Kato, 1963*a,b,c*, 1964*a,b*; Bonse, 1964; Kambe, 1965; Wilkens, 1966; Takagi, 1962, 1969; Balibar & Authier, 1967; Taupin, 1964; Chukhovskii & Shtolberg, 1970; Afanas'ev & Kohn, 1971; Howie & Whelan, 1961; Dederichs, 1966, 1967; and probably others). All but Dederichs's work appear to be phenomenological extensions of classical (Ewald-Laue-Bethe) perfect crystal theory to imperfect crystals and, hence, only find applications in those cases in which distortions are small.

Recent developments using such a phenomenological approach have led to equations such as Takagi's (1962, 1969). In this paper, therefore, the aim is to study the relation between Takagi's equation and the more exact dynamical equation.

### 2. Dynamical scattering amplitude

The scattering amplitude for an X-ray beam striking a crystal at position **R** with initial momentum **k** and

\* The dynamical theory of diffraction has also been formulated for a perfect crystal, using quantum field theoretical techniques, by Ohtsuki & Yanagawa (1966) and Hannon & Trammell (1968, 1969).