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On the Systematic Absence of Magnetic Reflections of Neutron Diffraction*

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We point out that the possession of reversal operations, by a magnetic lattice, causes the extinction of certain classes of magnetic reflections of unpolarized neutrons. Accordingly, the observation of systematic absences of magnetic reflections can be interpreted to identify the reversal operations involved. However, certain systematic absences of magnetic reflections are not caused by individual reversal operations. Neither are they trivial in the interpretation, nor do they have counterparts in the X-ray diffraction. We give in detail the interpretation of the absence of the ($h00$)-type magnetic reflections and that of the absence of the ($hk0$) reflections. The result is applied to analyze the Debye–Scherrer neutron diffraction of $ZnCr_2O_4$ at liquid-helium temperature. We are able to conclude that on any cubic plane, whose normal is not in the direction of the sublattice magnetization, the 16 Cr ions within a magnetic unit cell divide themselves into two groups, each of 8; the moments in one group are opposite to those in the other.

When a vector (dipole), instead of a scalar (atom), is assigned to each site of a point lattice, the dipole lattice has fewer symmetry elements (repeating operations) than the atomic lattice, unless the dipole moments are all equal and parallel. The dipoles may be oriented along a preferred axis, or different preferred axes. In general, the symmetry elements of the dipole lattice form a subgroup of the space group of the atomic lattice. Some symmetry operations of the atomic lattice, when applied to the dipole lattice, may leave the latter with every dipole turned through the same angle. When this angle is 180°, the dipole lattice is brought into one with every dipole reversed in direction. We shall call such an operation, a reversal operation. Examples of these rather abstract statements are found in the antiferromagnetic lattices. In the MnO-type compounds (Shull, Strauser & Wollan, 1951), a translation through one-half of a cubic edge of a magnetic unit cell is a reversal operation, and in MnO_2 (Erickson, 1952), a translation from a corner site to the body center brings the magnetic lattice into coincidence with one with every dipole turned 90°.

For the case of X-ray diffraction, lattice centerings (non-primitive lattices), screw axes, and glide planes cause extinctions in different classes of reflections. Consequently, the presence of these repeating operations of the atomic lattice is identified respectively by the corresponding systematic absences of reflections observed in diffraction patterns. A similar situation exists for the magnetic diffraction of unpolarized neutrons. (For a review of this field, see Bacon, 1955.) The unit cell of the dipole lattice (or the magnetic unit cell) is determined by the repeating operations. A reversal operation has the effect of extinguishing a certain class of magnetic reflections. Accordingly, the observation of the systematic absence of certain reflections may be interpreted to identify the corresponding operations. For example, we note that in the Debye–Scherrer pattern of the MnO-type compounds, the Miller indices of each of the magnetic reflections which have non-vanishing intensity are all odd numbers. It is this observation that leads us to conclude that a translation through one-half of a cubic edge of the magnetic unit cell is a reversal operation. Other examples may be found in almost every neutron diffraction pattern of antiferromagnetic lattices. A diffractionist will have no trouble in constructing a table of all the possible reversal operations and their corresponding absences of reflections. (A similar table for X-ray diffraction, including the lattice centerings, screw axes, and glide planes of atomic lattices has been given in several texts, e.g. Buerger, 1942.) However, certain possible systematic absences of magnetic reflections are not caused by individual reversal operations. These are neither trivial in the interpretation nor have counterparts in X-ray diffraction. A number of them were discovered when the author made an attempt to analyze the Debye–Scherrer pattern of $ZnCr_2O_4$ (Goldman, Hastings & Corliss, 1954) at liquid-helium temperature. As a result, an important feature of the antiferromagnetic lattice of this compound was revealed by the extinction of all the magnetic diffraction lines of the ($h00$) type.

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Let us recall that the intensity of magnetic diffraction of unpolarized neutrons is given by

$$I = |\mathbf{F}|^2\,, \tag{1}$$

where the (vector) amplitude

$$\mathbf{F}(hkl) = c \sum_j^{(\text{m.u.c.})} m_j f_j(\theta)\mathbf{q}_j \exp i2\pi(hx_j+ky_j+lz_j)\,, \tag{2}$$

with

$$\mathbf{q}_j(hkl) = \mathbf{e}(hkl)\{\mathbf{e}(hkl)\cdot\mathbf{e}_j\}-\mathbf{e}_j\,. \tag{3}$$

The summation $\sum_j^{(\text{m.u.c.})}$ is taken over all the magnetic ions in the magnetic unit cell. m_j and f_j are respectively the moment and the form factor of the jth magnetic ion, and c is a constant. f_j is a function of the Bragg angle θ. For coherent scattering m_j is proportional to S_j instead of $\{S_j(S_j+1)\}^{\frac{1}{2}}$, where S_j is the spin quantum number of the jth magnetic ion. $\mathbf{e}(hkl)$ and $\mathbf{e}_j$ are respectively the unit vector normal to the (hkl) plane and that in the direction of the jth moment. In most cases, there exists a single preferred axis, i.e. $\mathbf{e}_j = \pm\mathbf{e}$, and (2) reduces to

$$F(hkl) = cq(hkl) \sum_j^{(\text{m.u.c.})} (\pm m_j) f_j \exp i2\pi(hx_j+ky_j+lz_j)\,, \tag{4}$$

where $q(hkl)$ is the sine of the angle between $\mathbf{e}(hkl)$ and $\mathbf{e}$. The $+$ and $-$ signs before m_j must be chosen according to whether $\mathbf{e}_j = \mathbf{e}$ or $-\mathbf{e}$. For our present purpose let us consider the $(h00)$ reflections.

$$\begin{aligned} F(h00) &= c \sin(\mathbf{e}_x \wedge \mathbf{e}) \sum_j^{(\text{m.u.c.})} (\pm m_j) f_j \exp i2\pi hx_j \\ &= c \sin(\mathbf{e}_x \wedge \mathbf{e}) \sum_{x_\alpha}^{(\text{m.u.c.})} \left\{ \sum_{x_j=x_\alpha}^{(\text{m.u.c.})} (\pm m_j) f_j \right\} \exp i\, 2\pi hx_\alpha\,, \end{aligned} \tag{5}$$

where $\mathbf{e}_x$ is the unit vector in the direction of x axis and $\sin(\mathbf{e}_x \wedge \mathbf{e})$ is simply $q(h00)$. The summation $\sum_j^{(\text{m.u.c.})}$ is carried out by first summing over ions in a plane on which $x = \text{const.} \times x_\alpha$ and then summing over the different x_α planes. Assuming that the same form factor, or at least an average one, may be used for the magnetic ions, we obtain the relation

$$\sin(\mathbf{e}_x \wedge \mathbf{e}) \sum_{x_j=x_\alpha} (\pm m_j) \propto \frac{1}{c} \sum_h \frac{F(h00)}{f(\theta)} \exp(-i2\pi hx_\alpha) \tag{6}$$

by making a Fourier inversion. Therefore, when all the $(h00)$ reflections are absent we must have

$$\sin(\mathbf{e}_x \wedge \mathbf{e}) \sum_{x_j=x_\alpha} (\pm m_j) = 0\,; \tag{7}$$

i.e. either

$$\sum_{x_j=x_\alpha} (\pm m_j) = 0\,, \tag{8}$$

or

$$\mathbf{e} \,/\!/\, \mathbf{e}_x\,. \tag{9}$$

Equation (8) means that the sum of the magnetic moments of the ions on an $x = \text{const.}$ plane is zero. If the magnetic ions are all of the same kind or have equal moments, we must have equal numbers of moments in the opposite directions in an $x = \text{const.}$ plane, thus forming an antiferromagnetic sheet.

Similarly, we have

$$\begin{aligned} F(hk0) = cq(hk0) \sum_{\substack{x_\alpha \\ y_\alpha}}^{(\text{m.u.c.})} \Big\{ \sum_{\substack{x_j=x_\alpha \\ y_j=y_\alpha}} (\pm m_j) f_j(\theta) \Big\} \\ \times \exp i2\pi(hx_\alpha+ky_\alpha)\,. \end{aligned} \tag{10}$$

When the same form factor, or at least an average one, may be used for the magnetic ions, we have, by making a Fourier inversion,

$$\begin{aligned} \sum_{\substack{x_j=x \\ y_j=y}} (\pm m_j) \propto \frac{1}{c} \sum_{h,k}{}' \{F(hk0)/q(hk0)f(\theta)\} \\ \times \exp[-i2\pi(hx_\alpha+ky_\alpha)]\,, \end{aligned} \tag{11}$$

where the summation $\sum'_{h,k}$ is taken over all values of h and k except those for which $q(hk0) = 0$. Therefore, if all the $(hk0)$ reflections are absent, we have

$$\sum_{\substack{x_j=x_\alpha \\ y_j=y_\alpha}} (\pm m_j) = 0\,; \tag{12}$$

i.e. the sum of the moments of magnetic ions on a linear array in the z direction is zero. If the ions are all of the same kind or have equal moments we must have equal numbers of moments in opposite directions on a line in the z direction. In Table 1 we list the systematic absences and their interpretations considered above. Their applications to the Debye–Scherrer pattern are included.

The magnetic unit cell (m.u.c.) of $ZnCr_2O_4$, which has a normal spinel structure, has cubic edges twice as large as those of its chemical unit cell. Each m.u.c. contains 128 Cr ions. They are distributed on 8 cubic planes with 16 on each of them. In principle, the magnetic structure can be determined by adjusting a hypothetic model with the observed line intensity. The method is tedious when applied to the present case, and the result when concluded would be ambiguous. Fortunately, we find that in the Debye–Scherrer pattern of $ZnCr_2O_4$, the magnetic reflection lines of the $(h00)$ type are absent. Therefore, $ZnCr_2O_4$ must have a magnetic lattice such that, on any cubic plane whose normal is not in the direction of the sublattice magnetization, the 16 Cr ions within a magnetic unit cell divide themselves into two groups, each of 8; the moments in one group are opposite to those in the other. As a result, it is sufficient to conclude that $ZnCr_2O_4$ is antiferromagnetic at liquid-helium temperature. On the other hand, the Debye–Scherrer

Table 1. *The interpretation of certain systematic absences of magnetic reflections**

	Absent reflections	Interpretation
Single-crystal diffraction	All $(h00)$ reflections†	The sum of the magnetic moments of the ions on every $x =$ const. plane is zero: i.e. the magnetic lattice consists of antiferromagnetic sheets or The magnetic moments are either parallel or antiparallel to the x axis
	All $(hk0)$ reflections‡	The sum of the magnetic moments of the ions forming a linear chain along the direction of z axis is zero: i.e. the magnetic lattice consists of antiferromagnetic arrays
Debye–Scherrer diffraction	All $(h00)$ lines	The sum of magnetic moments of the ions on every $x =$ const. plane, every $y =$ const. plane and every $z =$ const. plane is zero or The sum of magnetic moments of the ions on every $x =$ const. plane and every $y =$ const. plane is zero and the moments are either parallel or antiparallel to the z axis
	All $(hk0)$ lines	The sum of magnetic moments of the ions on every linear chain along the x, y, and z direction is zero

* Assuming that all the magnetic ions are of the same kind and that their moments are either parallel or antiparallel to a certain direction.

† Similar interpretation applies to the absence of $(0k0)$ or $(00l)$ reflections.

‡ Similar interpretation applies to the absence of $(0kl)$ or $(h0l)$ reflections.

pattern of $ZnFe_2O_4$ (Corliss & Hastings, 1954) at very low temperatures is remarkably different from that of $ZnCr_2O_4$. The data of Corliss & Hastings indicate an appreciable intensity for the (200) magnetic reflection line. Corliss & Hastings (to appear) suggested an antiferromagnetic structure after carrying out a detailed analysis of the Debye–Scherrer intensity.

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