# Nuclear Magnetic Resonance in Crystals

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The general problem of crystal structure analysis by means of nuclear magnetic resonance is examined from the point of view of Van Vleck's theory for the second moment of the resonance absorption as applied to single crystals. Assuming only dipolar interactions to be important, and assuming a rigid lattice, a procedure is described for acquiring and analyzing the experimental second moments. It is shown that the second moment may be completely described by fifteen parameters in the most general type of crystal and thus only fifteen structural parameters can be uniquely determined from second moment data. The fifteen experimental parameters are related to fifteen sums over internuclear coordinates. The fifteen lattice sums must be equal to the corresponding theoretical lattice sums (from Van Vleck's theory) for the correct crystal structure. Thus a trial-and-error technique may be employed to determine nuclear coordinates. If the structure is known approximately, formulae are presented by means of which one may find the adjustments required in the nuclear coordinates of the trial structure. The calculations are well suited to programming on a high-speed digital computer.

## 1. Introduction

For many years X-ray diffraction has been the most important method available for the determination of the structure of crystals and it seems unlikely that this situation will change in the near future. However, there are certain problems in crystallography for which the X-ray technique is not well suited. Nuclear magnetic resonance (NMR) has been shown to offer a possible means of handling some of these difficult cases but NMR has been employed only in rather specific types of crystallographic problems. The most widely used technique is based on the analysis of fine structure characteristic of groups containing two, three, or four nuclei. However, this procedure may be applied only when the intra-group distances are much shorter than the inter-group distances. It is the purpose of the present paper to consider the problem of crystal structure determination by NMR from a point of view which is not dependent upon the existence of such groups of nuclei.

The discussion will be based upon the theory of Van Vleck (1948). In this theory the central quantity is the second moment, $\Delta H_2^2$, of the NMR absorption:

$$\Delta H_2^2 = \int H^2 f(H) \, dH \Big/ \int f(H) \, dH , \qquad (1)$$

where $f(H)$ is the absorption intensity at magnetic field $H$. Van Vleck showed that this quantity can be calculated from a knowledge of certain fundamental (and well known) constants and the nuclear coordinates in the lattice. The problem treated here is, conversely, to determine the nuclear coordinates from experimental NMR studies.

The discussion will be limited to the consideration of nuclei of spin $\frac{1}{2}$, e.g., $H^1$, $F^{19}$, and $P^{31}$. The lattice will be assumed to be rigid, and only dipolar inter-

actions are treated. It is assumed that $\Delta H_2^2$ data are available as a function of the orientation of a single crystal in the magnetic field.

The most important applications of the method probably involve hydrogen, which is almost invisible to X-rays. The nature of the dipolar interaction is such that near neighbors tend to dominate, with the result that short-range structural parameters can be determined accurately but long-range structural parameters can be found only with difficulty. In this respect the NMR method is complementary to the X-ray method. Normally, single crystals whose linear dimensions are of the order of one centimeter are necessary to produce adequate signals.

## 2. Theory

Van Vleck's theory (1948) for the second moment of a magnetic resonance, broadened by dipolar interactions alone, results in the expression:

$$\Delta H_2^2 = \Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} (3 \cos^2 \gamma_{kl} - 1)^2 , \qquad (2)$$

where only one magnetic species is present. In this formula $\Gamma = (\frac{3}{4}) I (I+1) g^2 \beta^2 / m$, where, $I$ is the nuclear spin, $m$ is the number of nuclei per unit cell at resonance, $\gamma_{kl}$ is the angle between $\mathbf{r}_{kl}$ and $\mathbf{H}_0$, $\mathbf{r}_{kl}$ is the vector between nuclei $k$ and $l$, and $\mathbf{H}_0$ is the externally applied magnetic field. $g$ is the nuclear gyromagnetic ratio and $\beta$ is the nuclear magneton.

It is convenient to transform equation (2) in such a way that the lattice sums may be calculated for any selected orientation of the magnetic field. Let us define a coordinate system fixed in the crystal. Let the direction of $\mathbf{H}_0$ be defined by $\theta$ and $\varphi$ and let the
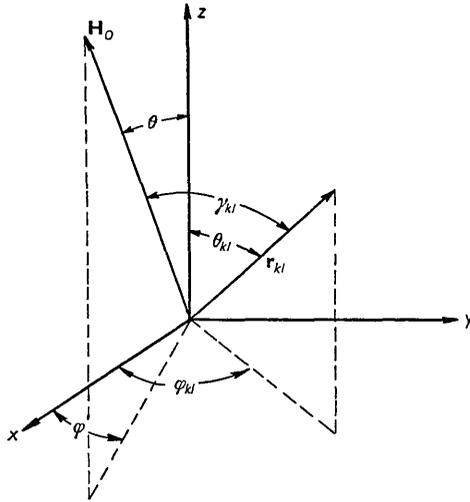
Fig. 1. Coordinate system employed in the transformation leading to equation (3).

direction of $r_{kl}$ be defined by $\theta_{kl}$ and $\varphi_{kl}$, see Fig. 1. Employing

$$\cos \gamma_{kl} = \cos \theta \cos \theta_{kl} + \sin \theta \sin \theta_{kl} \cos (\varphi - \varphi_{kl})$$

one finds that

$$(3 \cos^2 \gamma_{kl} - 1)^2 = 9a^4 + 9b^4c^4 + 9b^4d^4 + 54a^2b^2c^2 + 54a^2b^2d^2$$
$$+ 54b^4c^2d^2 + 108ab^3cd^2 + ab^3c^2d + 108a^2b^2cd$$
$$+ 36b^4cd^3 + 36b^4c^3d + 36ab^3c^3 + 36ab^3d^3$$
$$+ 36a^3bc + 36a^3bd - 6a^2 - 6b^2c^2 - 6b^2d^2 - 12abc$$
$$- 12abd - 12b^2cd + 1 , \qquad (3)$$

where

$$a = \cos \theta \cos \theta_{kl}; \qquad c = \cos \varphi \cos \varphi_{kl}$$
$$b = \sin \theta \sin \theta_{kl}; \qquad d = \sin \varphi \sin \varphi_{kl} .$$

In equation (3) each term is a product of a function of $\theta$ and $\varphi$ and a similar function of $\theta_{kl}$ and $\varphi_{kl}$. Thus the $\theta$ and $\varphi$ terms can be factored out of the individual terms and the sums computed for any crystal orientation. In computing sums such as these it is convenient to employ cartesian coordinates:

$$r_{kl}^2 = x_{kl}^2 + y_{kl}^2 + z_{kl}^2$$
$$\cos \theta_{kl} = z_{kl}/r_{kl}$$
$$\sin^2 \theta_{kl} = (x_{kl}^2 + y_{kl}^2)/r_{kl}^2$$
$$\cos^2 \varphi_{kl} = x_{kl}^2/(x_{kl}^2 + y_{kl}^2)$$
$$\sin^2 \varphi_{kl} = y_{kl}^2/(x_{kl}^2 + y_{kl}^2) .$$

One may write equation (1) in the form:

$$\Delta H_2^2 = A \cos^4 \theta + B \cos^2 \theta + C + (D \cos \varphi + E \sin \varphi)$$
$$\times \cos^3 \theta \sin \theta + (F \cos \varphi + G \sin \varphi) \cos \theta \sin \theta$$
$$+ (H \cos^2 \varphi + I \cos \varphi \sin \varphi + J \sin^2 \varphi) \cos^2 \theta \sin^2 \theta$$
$$+ (K \cos^2 \varphi + L \cos \varphi \sin \varphi + M \sin^2 \varphi) \sin^2 \theta$$
$$+ (N \cos^3 \varphi + O \cos^2 \varphi \sin \varphi + P \cos \varphi \sin^2 \varphi + Q \sin^3 \varphi)$$
$$\times \cos \theta \sin^3 \theta + (R \cos^4 \varphi + S \cos^3 \varphi \sin \varphi + T \cos^2 \varphi \sin^2 \varphi$$
$$+ U \cos \varphi \sin^3 \varphi + V \sin^4 \varphi) \sin^4 \theta , \qquad (4)$$

where the $A, B, \ldots, V$ are proportional to lattice sums. These quantities are defined in Appendix I.

The first step in the reduction of the NMR data is to find the lattice sums. Of the 22 coefficients that appear in equation (4) only 15 are independent.[*] Appendix II gives seven of them in terms of the other 15 sums. If this elimination be made in equation (4) then we have an equation of the form

$$\Delta H_2^2 = \sum_{i=1}^{15} k_i f_i(\theta, \varphi) .$$

As long as we have made at least 15 *independent* measurements we may use the least-squares method of determining the coefficients $k_i$ by minimizing

$$\sum_{\substack{\text{all} \\ \text{data}}} \left\{ \Delta H_2^2 (\text{exp}) - \sum_{i=1}^{15} k_i f_i(\theta, \varphi) \right\}^2 .$$

This leads to the 15 'normal equations'

$$\sum_{\substack{\text{all} \\ \text{data}}} \left\{ \Delta H_2^2 (\text{exp}) - \sum_{i=1}^{15} k_i f_i(\theta, \varphi) \right\} f_j(\theta, \varphi) = 0 ,$$

where $j = 1, 2, \ldots, 15$.

The problem of solving these fifteen 'normal equations' is apt to be very difficult in practice, so that it is worth considering more indirect methods. Furthermore, the sufficient conditions that enough *independent* data are available are not obvious from the preceding discussion. Thus, it is desirable to seek a form for equation (4) which enables one to discern the conditions for *independence* of measurements.

Equation (4) may be written as a double Fourier series in $\theta$ and $\varphi$ in the form

$$\Delta H_2^2 =$$
$$\sum_{n=0}^{4} \sum_{m=0}^{4} \{ a_{n,m} \cos n\theta \cos m\varphi + a_{n,m+4} \cos n\theta \sin m\varphi$$
$$\times a_{n+4,m} \sin n\theta \cos m\varphi + a_{n+4,m+4} \sin n\theta \sin m\varphi \} . \qquad (5)$$

There are 23 non-zero $a_{n,m}$, of which 15 independent ones are tabulated in Appendix III while Appendix IV gives eight redundant conditions. Appendix V contains the resolution of Appendix III. If, now, $\Delta H_2^2$ is measured for several fixed values of $\varphi$ at equal spaces ($\Delta \theta$) in $\theta$, covering 0 to $2\pi$, we can apply the usual orthogonality conditions and obtain

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[*] It can be shown that there are no more than 15 independent lattice sums in equation (4) by writing down the 22 terms: $1, x^2, y^2, z^2, xy, xz, zy, x^4, x^3y, x^2y^2, xy^3, y^4, x^3z, x^2yz, xy^2z, y^3z, x^2z^2, xyz^2, y^2z^2, z^4, xz^3, yz^3$; and eliminating those containing $z^2$ by means of $z^2 = r^2 - x^2 - y^2$. Seven terms can be eliminated in this way and no new terms are introduced. As all the information resides in 15 independent lattice sums it is desirable to discard seven of the sums. This must be done in such a way that each sum of the group discarded must be capable of being expressed in terms of the 15 sums retained.

$a_{00}+a_{02}\cos 2\varphi_p+3a_{44}\cos 4\varphi_p+a_{06}\sin 2\varphi_p$

$$-(3/4)a_{28}\sin 4\varphi_p = g(\varphi_p, 0)$$

$a_{20}-(a_{02}+a_{42})\cos 2\varphi_p-4a_{44}\cos 4\varphi_p+a_{26}\sin 2\varphi_p$

$$+a_{28}\sin 4\varphi_p = g(\varphi_p, 2)$$

$a_{40}+a_{42}\cos 2\varphi_p+a_{44}\cos 4\varphi_p-(a_{26}+a_{06})\sin 2\varphi_p$

$$-(a_{28}/4)\sin 4\varphi_p = g(\varphi_p, 4)$$

$a_{61}\cos \varphi_p+a_{63}\cos 3\varphi_p+a_{65}\sin \varphi_p-2a_{87}\sin 3\varphi_p$

$$= g(\varphi_p, 6)$$

$a_{81}\cos \varphi_p-(a_{63}/2)\cos 3\varphi_p+a_{85}\sin \varphi_p+a_{87}\sin 3\varphi_p$

$$= g(\varphi_p, 8)$$

where                                                                           (6)

$$g(\varphi_p, n) = (\Delta\theta/\pi)\sum_{i=1}^{2\pi/\Delta\theta} \Delta H_2^2(\varphi_p, i\Delta\theta)\cos (in\Delta\theta)$$

$$\text{for } n = 0, \ldots, 4$$

and

$$g(\varphi_p, n) = (\Delta\theta/\pi)\sum_{i=1}^{2\pi/\Delta\theta} \Delta H_2^2(\varphi_p, i\Delta\theta)\sin [i(n-4)\Delta\theta]$$

$$\text{for } n = 5, \ldots, 8 .$$

Similarly, if $\Delta H_2^2$ is measured for several fixed values of $\theta$ at equal spaces $(\Delta\varphi)$ in $\varphi$, we obtain

$a_{00}+a_{20}\cos 2\theta_p+a_{40}\cos 4\theta_p = h(\theta_p, 0)$

$a_{81}\sin 4\theta_p+a_{61}\sin 2\theta_p = h(\theta_p, 1)$

$a_{02}(1-\cos 2\theta_p)+a_{42}(\cos 4\theta_p-\cos 2\theta_p) = h(\theta_p, 2)$

$a_{63}[\sin 2\theta_p-(1/2)\sin 4\theta_p] = h(\theta_p, 3)$

$a_{44}(3-4\cos 2\theta_p+\cos 4\theta_p) = h(\theta_p, 4)$

$a_{06}(1-\cos 4\theta_p)+a_{26}(\cos 2\theta_p-\cos 4\theta_p) = h(\theta_p, 5)$

$a_{65}\sin 2\theta_p+a_{85}\sin 4\theta_p = h(\theta_p, 6)$

$a_{87}(\sin 4\theta_p-2\sin 2\theta_p) = h(\theta_p, 7)$

$a_{28}[\cos 2\theta_p-(1/4)\cos 4\theta_p-(3/4)] = h(\theta_p, 8) ,$      (7)

where the $h(\theta_p, m)$ sums are defined in analogy with the $g(\varphi_p, n)$ given above.

Experimentally it is easier to measure a $\theta$-dependence at constant $\varphi$ than a $\varphi$-dependence at constant $\theta$. That is to say, it is preferable for experimental reasons to use cylindrical samples, for such specimens best fill the conventional sort of coil and yield the best signal strength.

Although the set of measurements used to determine the $a_{nm}$ is arbitrary we must take pains that enough independent data are available. From equations (6) it can be shown that it is not possible to determine the 15 $a_{nm}$ uniquely from $\theta$-dependences at any three constant values of $\varphi_p$, even though there are 15 equations.

A sufficient set of measurements consists of $\theta$-dependences at $\varphi_p = 0$, $\pi/4$, $\pi/2$ and a $\varphi$-dependence at $\theta_p = \pi/2$. The lattice sums are readily calculated in terms of this set and the results are tabulated in Appendix VI. Note that four oriented single crystals are necessary for this type of analysis.

In addition to the direct determination of the $a_{nm}$ the preceding analysis yields a number of sums over the experimental data which must be identically zero.

$g(\varphi_p, n) = 0$ for $n = 1, 3, 5, 7$ for any $\theta$-dependence at constant $\varphi$ and $h(\pi/2, m) = 0$ for $m = 1, 3, 6, 7$. These identities should be useful in assessing the accuracy of the measurements and could be used to smooth the data.

The second part of the reduction of the NMR data is to find the lattice constants. To do this we now consider the computation of the lattice sums $W$ for a general sub-lattice described by the fundamental translation vectors, $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. There is a point of the sub-lattice at

$$\mathbf{r}_l = n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c} ,$$

where $n_1$, $n_2$, $n_3$ are arbitrary integers. The sums are to be computed relative to the point $(x_k, y_k, z_k)$. Nine parameters are necessary to specify a general (triclinic) sub-lattice completely and we designate these as $a_0$, $\ldots$, $c_0$ where

$$\mathbf{a} = a_0\mathbf{i}+a_0'\mathbf{j}+a_0''\mathbf{k}$$
$$\mathbf{b} = b_0''\mathbf{i}+b_0\mathbf{j}+b_0'\mathbf{k}$$
$$\mathbf{c} = c_0'\mathbf{i}+c_0''\mathbf{j}+c_0\mathbf{k}$$

and $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors along the $X$-, $Y$-, and $Z$-axes (see Fig. 2).
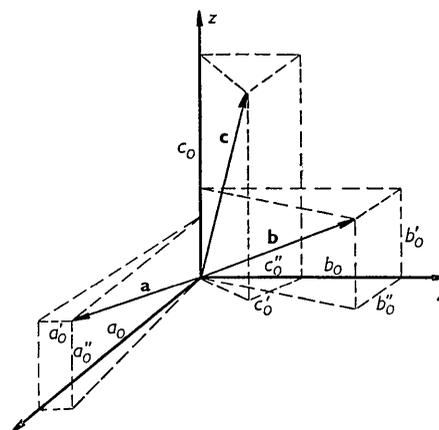


Fig. 2. The relationship of the crystallographic parameters to the cartesian coordinates.

Any of the lattice sums $A$, $B$, $\ldots$, $V$ may be written as

$$W = v\Gamma\sum_{k=1}^{m}\sum_{l} x_{kl}^u y_{kl}^v z_{kl}^w r_{kl}^{-(6+u+v+w)} ,$$      (8)

where $v$, $u$, $v$, and $w$ are known integers. Equation (8) may be written as

$$W = v\Gamma\sum_{k=1}^{m}\sum_{n_1}\sum_{n_2}\sum_{n_3}$$
$$\times \{(x_k-n_1a_0-n_2b_0''-n_3c_0')^u(y_k-n_1a_0'-n_2b_0-n_3c_0'')^v$$
$$\times (z_k-n_1a_0''-n_2b_0'-n_3c_0)^w r_{kl}^{-(6+u+v+w)}\} ,$$      (9)

where

$$r_{kl}^2 = (x_k-n_1a_0-n_2b_0''-n_3c_0')^2$$
$$+ (y_k-n_1a_0'-n_2b_0-n_3c_0'')^2+(z_k-n_1a_0''-n_2b_0'-n_3c_0)^2 .$$

We first postulate a trial structure on the basis of other experiments and intuition, i.e., we assume values for $x_k, \ldots, c_0''$. Then, the 15 lattice sums $W$ are calculated by means of equation (9). These trial sums, $W_t$, are then compared with the sums obtained experimentally, $W_e$:

$$\delta W = W_e - W_t . \tag{10}$$

The next problem is to determine adjustments in the structural parameters, $\delta x, \ldots, \delta c_0''$, which will minimize the $\delta W$. This may be done as follows. By direct partial differentiation one obtains:

$$(\partial W/\partial x_k) = \nu\Gamma \sum_{k=1}^{m} \sum_{n_1} \sum_{n_2} \sum_{n_3}$$

$$\times \{[u-(6+u+v+w)r_{kl}^{-k}(x_k-n_1a_0-n_2b_0''-n_3c_0')^2]$$

$$\times (x_k-n_1a_0-n_2b_0''-n_3c_0')^{u-1}(y_k-n_1a_0'-n_2b_0-n_3c_0')^v$$

$$\times (z_k-n_1a_0''-n_2b_0'-n_3c_0)^w r_{kl}^{-(6+u+v+w)}\}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$(\partial W/\partial c_0'') = \nu\Gamma \sum_{k=1}^{m} \sum_{n_1} \sum_{n_2} \sum_{n_3}$$

$$\times \{[(6+u+v+w)r_{kl}^{-2}(y_k-n_1a_0'-n_2b_0-n_3c_0'')^2 - v]$$

$$\times (x_k-n_1a_0-n_2b_0''-n_3c_0')^{u}(y_k-n_1a_0'-n_2b_0-n_3c_0')^{v-1}$$

$$\times (z_k-n_1a_0''-n_2b_0'-n_3c_0)^w n_3 r_{kl}^{-(6+u+v+w)}\} .$$

Therefore by

$$dW = \sum_{k=1}^{m} (\partial W/\partial x_k)dx_k + \ldots + (\partial W/\partial c_0'')dc_0''$$

we have

$$(\delta W/\nu\Gamma) = \sum_{k=1}^{m} \delta x_k \Sigma\Sigma\Sigma\{\ \} + \ldots + \delta c_0'' \Sigma\Sigma\Sigma\Sigma\{\ \} . \tag{11}$$

There are 15 equations of the form of equation (11) and these may be used to solve for the parametric adjustments $\delta x, \ldots, \delta c''$. If there are more than 15 parameters to be adjusted additional conditions are required if a unique solution is to be obtained.* This self-consistent procedure leads to an improved trial structure and the process is repeated until the $\delta W$ are minimized.

When other nuclear magnetic species are present in the structure equation (2) must be augmented by a second term to cover the foreign nuclei. Van Vleck (1948) showed this term to be

$$\sum_{k=1}^{m} \sum_{f} \Gamma_f r_{kf}^{-6} (3 \cos^2 \gamma_{kf} - 1)^2 ,$$

where $\Gamma_f = (1/3)I_f(I_f+1)g_f^2\beta^2/m$. The extension of the foregoing analysis to include this term is obvious.

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* For example, X-ray analysis may yield very accurate values for the unit-cell dimensions $a_0, \ldots, c_0''$ but no information regarding the positional parameters $x_k, y_k, z_k$. In such a case one would adjust only the parameters $x_k, \ldots$; i.e. assume that $\delta a_0, \ldots$ are zero.

## 3. Conclusions

We have seen that NMR second moment data for single crystals may be used to determine crystal structures provided only dipolar forces are important and the lattice is rigid. We will now consider the quantity of structural information which may in general be obtained.

The sums given in equation (9) may be written in terms of sub-sums:

$$W = \sum_{k=1}^{m} \sum_{s=1}^{m} W^{(ks)} ,$$

where $W^{(kk)}$ represents the $W$ sum over the $k$ sub-lattice and $W^{(ks)}$ represents the $W$ sum over the $s$ sub-lattice, all sums computed about the point $(x_k, y_k, z_k)$. Thus, there are $m^2$ sub-sums to be computed for each of the 15 equations. However,

$$W^{(11)} = W^{(22)} = \ldots = W^{(mm)}$$

and

$$W^{(ij)} = W^{(ji)}$$

so there are only $[m(m-1)/2]+1$ distinct sub-sums to be computed. The calculation of so many lattice sums is exceedingly tedious for most crystals. However, the problem is well suited to solution by high-speed electronic digital computers which will eliminate much of the human labor.

The general lattice requires nine parameters for its description, i.e., the components of $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, and this description serves to locate one nucleus per unit cell. Three additional parameters are required for every other nucleus (per unit cell) to be specified. As we have seen there are 15 lattice sums and thus 15 parametric adjustments can be made. Therefore, with no outside information available, NMR second moment analysis can uniquely determine a crystal which has no more than $[(15-9)/3]+1 = 3$ nuclei per unit cell.

Thus we must draw upon all the outside information at our disposal. X-ray diffraction data is probably the most likely source of such information, and in complex structures it may be that it is not practical to begin the NMR study until a complete X-ray analysis has been carried through. X-ray data can be quite useful, however, even if a structure analysis has not been attempted. For example, knowledge of the lattice type, unit-cell dimensions, and the number of molecules per unit-cell greatly simplifies the initial steps. Also, such information increases the number of parameters that the NMR method described herein can cope with, e.g. if the cell dimensions are known the NMR method can determine six nuclei per unit cell as opposed to three when no data are available at the outset.

From rather superficial aspects of the NMR spectra one may often obtain structural information which is highly pertinent to the second moment analysis. For example (Pake, 1948), when protons occur in pairs, as in hydrates, each proton sees predominately the

local field due to its nearest neighbor. This results in a characteristic doublet structure which yields the proton–proton separation and the orientation of the inter-nuclear vector. Thus any adjustment of the parameters of one of the nuclei must be accompanied by known adjustments of the other.

When the space group of the crystal is known it may be possible to establish that certain of the lattice sums are identically equal to zero by symmetry. This analysis is direct and obvious for the sub-sums $W^{(kk)}$ because all the symmetries of the crystal also apply to the sub-lattice. For example, if the crystal possesses a plane of symmetry normal to the $Z$-axis it is apparent, by inspection, that the sub-sums $D^{(kk)}$, $E^{(kk)}$, $F^{(kk)}$, $G^{(kk)}$, $N^{(kk)}$, $O^{(kk)}$, and $P^{(kk)}$ are zero. The sub-sums $W^{(ks)}$ cannot be dealt with such dispatch. In order that use can be made of symmetry the point $(x_k, y_k, z_k)$ must lie on a plane of symmetry, on an axis of rotation, or on an inversion point of the sub-lattice $s$.

## APPENDIX I

### Definition of 22 fundamental lattice sums (equation (4))

$$A = 9\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos^4 \theta_{kl} = 9\Gamma \sum_{k=1}^{m} \sum_{l} z_{rl}^4 r_{rl}^{-10}$$

$$B = -6\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos^2 \theta_{kl} = -6\Gamma \sum_{k=1}^{m} \sum_{l} z_{kl}^2 r_{kl}^{-8}$$

$$C = \Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6}$$

$$D = 36\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos^3 \theta_{kl} \sin \theta_{kl} \cos \varphi_{kl}$$
$$= 36\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl} z_{kl}^3 r_{kl}^{-10}$$

$$E = 36\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos^3 \theta_{kl} \sin \theta_{kl} \sin \varphi_{kl}$$
$$= 36\Gamma \sum_{k=1}^{m} \sum_{l} y_{kl} z_{kl}^3 r_{kl}^{-10}$$

$$F = -12\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos \theta_{kl} \sin \theta_{kl} \cos \varphi_{kl}$$
$$= -12\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl} z_{kl} r_{kl}^{-8}$$

$$G = -12\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos \theta_{kl} \sin \theta_{kl} \sin \varphi_{kl}$$
$$= -12\Gamma \sum_{k=1}^{m} \sum_{l} y_{kl} z_{kl} r_{kl}^{-8}$$

$$H = 54\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos^2 \theta_{kl} \sin^2 \theta_{kl} \cos^2 \varphi_{kl}$$
$$= 54\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl}^2 z_{kl}^2 r_{kl}^{-10}$$

$$I = 108\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos^2 \theta_{kl} \sin^2 \theta_{kl} \cos \varphi_{kl} \sin \varphi_{kl}$$
$$= 108\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl} y_{kl} z_{kl}^2 r_{kl}^{-10}$$

$$J = 54\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos^2 \theta_{kl} \sin^2 \theta_{kl} \sin^2 \varphi_{kl}$$
$$= 54\Gamma \sum_{k=1}^{m} \sum_{l} y_{kl}^2 z_{kl}^2 r_{kl}^{-10}$$

$$K = -6\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \sin^2 \theta_{kl} \cos^2 \varphi_{kl}$$
$$= -6\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl}^2 r_{kl}^{-8}$$

$$L = -12\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \sin^2 \theta_{kl} \cos \varphi_{kl} \sin \varphi_{kl}$$
$$= -12\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl} y_{kl} r_{kl}^{-8}$$

$$M = -6\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \sin^2 \theta_{kl} \sin^2 \varphi_{kl}$$
$$= -6\Gamma \sum_{k=1}^{m} \sum_{l} y_{kl}^2 r_{kl}^{-8}$$

$$N = 36\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos \theta_{kl} \sin^3 \theta_{kl} \cos^3 \varphi_{kl}$$
$$= 36\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl}^3 z_{kl} r_{kl}^{-10}$$

$$O = 108\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos \theta_{kl} \sin^3 \theta_{kl} \cos^2 \varphi_{kl} \sin \varphi_{kl}$$
$$= 108\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl}^2 y_{kl} z_{kl} r_{kl}^{-10}$$

$$P = 108\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos \theta_{kl} \sin^3 \theta_{kl} \cos \varphi_{kl} \sin^2 \varphi_{kl}$$
$$= 108\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl} y_{kl}^2 z_{kl} r_{kl}^{-10}$$

$$Q = 36\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \cos \theta_{kl} \sin^3 \theta_{kl} \sin^3 \varphi_{kl}$$
$$= 36\Gamma \sum_{k=1}^{m} \sum_{l} y_{kl}^3 z_{kl} r_{kl}^{-10}$$

$$R = 9\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \sin^4 \theta_{kl} \cos^4 \varphi_{kl} = 9\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl}^4 r_{kl}^{-10}$$

$$S = 36\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \sin^4 \theta_{kl} \cos^3 \varphi_{kl} \sin \varphi_{kl}$$
$$= 36\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl}^3 y_{kl} r_{kl}^{-10}$$

$$T = 54\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \sin^4 \theta_{kl} \cos^2 \varphi_{kl} \sin^2 \varphi_{kl}$$
$$= 54\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl}^2 y_{kl}^2 r_{kl}^{-10}$$

$$U = 36\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \sin^4 \theta_{kl} \cos \varphi_{kl} \sin^3 \varphi_{kl}$$
$$= 36\Gamma \sum_{k=1}^{m} \sum_{l} x_{kl} y_{kl}^3 r_{kl}^{-10}$$

$$V = 9\Gamma \sum_{k=1}^{m} \sum_{l} r_{kl}^{-6} \sin^4 \theta_{kl} \sin^4 \varphi_{kl} = 9\Gamma \sum_{k=1}^{m} \sum_{l} y_{kl}^4 r_{kl}^{-10}$$

## APPENDIX II

### 7 relations between fundamental lattice sums

$$K = -B - 6C - M$$
$$H = 27C - 3A - 3R + 3V + 9M$$
$$T = 27C + 9B + 3A - 3R - 3V$$

$$P = -9F - 3D - 3N$$
$$O = -9G - 3E - 3Q$$
$$I = -9L - 3S - 3U$$
$$J = -27C - 9B - 3A + 3R - 3V - 9M$$

## APPENDIX III

### 15 non-zero Fourier coefficients in equation (5) expressed by fundamental lattice sums

$$a_{00} = (7B/64) + (9A/64) + (49C/64)$$
$$a_{02} = (15C/8) + (5B/16) - (3R/16) + (3V/16) + (5M/8)$$
$$a_{06} = -(5L/16) - (3S/32) - (3U/32)$$
$$a_{20} = (5A/16) + (3B/16) - (3C/16)$$
$$a_{26} = -(L/4) - (S/8) - (U/8)$$
$$a_{28} = -(S/16) + (U/16)$$
$$a_{40} = (35A/64) + (45B/64) + (27C/64)$$
$$a_{42} = -(27C/8) - (9B/16) + (7R/16) - (7V/16) - (9M/8)$$
$$a_{44} = (R/16) + (V/16) - (27C/64) - (9B/64) - (3A/64)$$
$$a_{61} = (D/16) - (F/16)$$
$$a_{63} = (N/4) + (9F/16) + (3D/16)$$
$$a_{65} = (E/16) - (G/16)$$
$$a_{81} = (7D/32) + (9F/32)$$
$$a_{85} = (7E/32) + (9G/32)$$
$$a_{87} = (9G/32) + (3E/32) + (Q/8)$$

## APPENDIX IV

### Eight redundant relations between the $a_{n,m}$ (equation (5))

| | |
|---|---|
| $a_{83} = -a_{63}/2$ | $a_{67} = -2a_{87}$ |
| $a_{08} = -3a_{28}/4$ | $a_{04} = 3a_{44}$ |
| $a_{48} = -a_{28}/4$ | $a_{24} = -4a_{44}$ |
| $a_{46} = -a_{26} - a_{06}$ | $a_{22} = -a_{02} - a_{42}$ |

## APPENDIX V

### Resolution of relations in Appendix III

$$A = (9a_{00}/4) + (21a_{20}/4) - (7a_{40}/4)$$
$$B = -(5a_{00}/2) - (23a_{20}/6) + (17a_{40}/6)$$
$$C = (5a_{00}/4) - (5a_{20}/12) - (a_{40}/12)$$
$$D = 2a_{81} + 9a_{61}$$
$$E = 2a_{85} + 9a_{65}$$
$$F = 2a_{81} - 7a_{61}$$
$$G = 2a_{85} - 7a_{65}$$
$$L = -8a_{06} - 6a_{26}$$

$$M = 8a_{44} - 2a_{42} - 2a_{02} - (a_{00}/4) - (7a_{20}/12) + (13a_{40}/12)$$
$$N = 4a_{63} - 6a_{81} + 9a_{61}$$
$$Q = 8a_{87} - 6a_{85} + 9a_{65}$$
$$R = 5a_{42} + 9a_{02} + 8a_{44} + (9a_{00}/4) - (15a_{20}/4) + (9a_{40}/4)$$
$$S = 8a_{06} + 10a_{26} - 8a_{28}$$
$$U = 8a_{06} + 10a_{26} + 8a_{28}$$
$$V = 8a_{44} - 5a_{42} - 9a_{02} + (9a_{00}/4) - (15a_{20}/4) + (9a_{40}/4)$$

## APPENDIX VI

### The 15 fundamental lattice sums expressed by an independent set of 15 functions $g(\varphi_p, n)$ (equation (16))

$$A = (15/4)g(0,0) + (21/4)g(0,2) + (7/4)g(0,4)$$
$$\quad - (7/4)g(\pi/2, 0) - (7/2)g(\pi/2, 4) + 2h(\pi/2, 4)$$
$$B = -(19/6)g(0,0) - (23/6)g(0,2) - (1/2)g(0,4)$$
$$\quad + (2/3)g(\pi/2, 0) + (10/3)g(\pi/2, 4) - (4/3)h(\pi/2, 4)$$
$$C = (5/12)g(0,0) - (5/12)g(0,2) - (1/4)g(0,4)$$
$$\quad + (5/6)g(\pi/2, 0) + (1/6)g(\pi/2, 4) - (2/3)h(\pi/2, 4)$$
$$D = 24\sqrt{(2)}g(\pi/4, 7) + 16\sqrt{(2)}g(\pi/4, 5) + 3g(\pi/2, 7)$$
$$\quad + 2g(\pi/2, 5) - 22g(0,7) - 7g(0,5)$$
$$E = -14\sqrt{(2)}g(\pi/4, 7) - 7\sqrt{(2)}g(\pi/4, 5) + 16g(\pi/2, 7)$$
$$\quad + 16g(\pi/2, 5) + 14g(0,7) + 7g(0,5)$$
$$F = -24\sqrt{(2)}g(\pi/4, 7) - 16\sqrt{(2)}g(\pi/4, 5) + 3g(\pi/2, 7)$$
$$\quad + 2g(\pi/2, 5) + 26g(0,7) + 9g(0,5)$$
$$G = 18\sqrt{(2)}g(\pi/4, 7) + 9\sqrt{(2)}g(\pi/4, 5) - 16g(\pi/2, 7)$$
$$\quad - 16g(\pi/2, 5) - 18g(0,7) - 9g(0,5)$$
$$L = 8g(\pi/4, 4) - h(\pi/2, 5) + 2h(\pi/2, 4)$$
$$M = (23/48)h(\pi/2, 4) + (11/6)g(\pi/2, 4) + (7/6)g(\pi/2, 0)$$
$$\quad - (1/3)g(0,4) - (7/12)g(0,2) - (17/12)g(0,0)$$
$$N = 24\sqrt{(2)}g(\pi/4, 7) + 16\sqrt{(2)}g(\pi/4, 5) + 3g(\pi/2, 7)$$
$$\quad + 2g(\pi/2, 5) - 30g(0,7) - 7g(0,5)$$
$$Q = -14\sqrt{(2)}g(\pi/4, 7) - 7\sqrt{(2)}g(\pi/4, 5) + 8g(\pi/2, 7)$$
$$\quad + 16g(\pi/2, 5) + 14g(0,7) + 7g(0,5)$$
$$R = -2h(\pi/2, 4) + (1/2)g(\pi/2, 4) - (3/2)g(\pi/2, 0)$$
$$\quad + (7/4)g(0,4) - (15/4)g(0,2) + (15/4)g(0,0)$$
$$S = -8g(\pi/4, 4) - h(\pi/2, 5) - 2h(\pi/2, 4) + 4h(\pi/2, 8)$$
$$U = -8g(\pi/4, 4) - h(\pi/2, 5) - 2h(\pi/2, 4) - 4h(\pi/2, 8)$$
$$V = -2h(\pi/2, 4) + (11/2)g(\pi/2, 4) + (15/2)g(\pi/2, 0)$$
$$\quad - (13/4)g(0,4) - (15/4)g(0,2) - (21/4)g(0,0)$$

### References

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