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Analysis of Nuclear Magnetic Resonance Line Shapes by Lattice Harmonics*

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The second (M_2) and fourth (M_4) moments of magnetic resonance absorption lines of nuclei in crystals resulting from dipolar and exchange interactions have been given by Van Vleck. The dependence of M_2 and M_4 on the orientation of the magnetic field in the crystal coordinate system may be rewritten in terms of lattice harmonics of the crystal point group. Only lattice harmonics belonging to the identity representation occur. The number of such functions, and hence the number of independent quantities needed to specify M_2 and M_4 have been determined for all 32 point groups. These numbers vary from 15 and 45 for triclinic C_1 symmetry to 2 and 4 for cubic O_h symmetry. M_2 and M_4 are given as a finite series of lattice harmonics of the crystal orientation, the coefficients of which are expressed as irreducible lattice sums. Application is made to available data on the resonance of F^{19} in CaF_2, Al^{27} in aluminum metal and H^1 in urea, $CO(NH_2)_2$; the effect of lattice vibrations on the moments of CaF_2 and Al are examined. The influence of an applied electric field of NMR moments and the use of lattice harmonics in other spectroscopics of the solid state are considered.

I. INTRODUCTION

THE shapes of magnetic resonance absorption lines of nuclei in crystals resulting from dipolar and exchange interactions may be characterized by the moments of the continuous wave absorption signal.[1] Likewise, free precession decay signals may be expressed in terms of the moments of the continuous wave absorption by means of a series expansion in powers of the time following a 90° pulse.[2] The moments are intimately related to the relative positions of magnetic nuclei in the crystal as shown by the calculations of Van Vleck[1] wherein the second and fourth moments were expressed as a function of the direction of the applied field relative to radii vectors between nuclei. These expressions, particularly that for the second moment, have been extensively used[3,4] in the determination of the relative positions of magnetic nuclei in crystals. Most applications have been concerned with crystals containing protons situated in groups of two or three since the analysis of the nuclear magnetic resonance signals is relatively simple in such cases. For more general situations, the problem of determining the positions of the nuclei in the crystal from the observed angular dependence of nuclear magnetic resonance signals on crystal orientation is a rather formidable one. One reason for this is that Van Vleck's expressions for the second and fourth moments are generally rather cumbersome for an arbitrary orientation of the crystal relative to the applied field. Furthermore, it has not been known exactly how much information could be extracted from the experimental moments—that is, whether it is possible to completely determine the relative positions of the magnetic nuclei from a given amount of experimental data. It is the purpose of the present work to show that these difficulties may be removed by rewriting the moments in terms of the lattice harmonics corresponding to the point group of the magnetic nuclei in the crystal under study. Lattice harmonics form a complete and orthonormal set of functions[5,6] which form a basis for the irreducible representations of the point group of the crystal and hence are ideally suited for expression of quantities which depend on the crystal orientation. In addition, it will be shown that only those lattice harmonics which belong to the identity representation of the crystal point group need to be considered; this result fixes the number of independent quantities needed to specify the moments.

In the next section some of the properties of moments and Van Vleck's calculation are reviewed. In the following two sections we consider the transformation properties of the second and fourth moments under coordinate rotations and rewrite Van Vleck's expressions in their most convenient and irreducible forms. The number of independent components for the 32 point groups are derived and tabulated along with vector coupling coefficients for spherical and lattice harmonics which are useful in the analytical expression of the moments. In Sec. V, the influence of the space group on the moments is considered and in the following section illustrations of the above theory for available experimental data on CaF_2, aluminum metal, and urea $CO(NH_2)_2$, are given.

In the final section, other possible applications of lattice harmonics in the angular dependence of magnetic resonance and optical spectra of crystals are briefly discussed.

II. MOMENT METHOD

The nth moment M_n of a nuclear magnetic resonance absorption spectrum with intensity $f(\omega)$ at an angular

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[2] I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

[3] E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, New York, 1958).

[4] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. 4.

[5] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

[6] D. G. Bell, Revs. Modern Phys. **26**, 311 (1954).

frequency ω is defined as follows[1]:

$$M_n=\int_{-\infty}^{\infty}(\omega-\omega_0)^n f(\omega)d\omega \bigg/ \int_{-\infty}^{\infty} f(\omega)d\omega. \qquad (1)$$

In the case of only dipolar or exchange interactions between nuclei and in the absence of quadrupolar interactions, ω_0 is the mean resonance frequency for which

$$\int_{-\infty}^{\infty}(\omega-\omega_0)f(\omega)d\omega=0$$

and generally all odd moments vanish in this situation.

Van Vleck[1] computed the second and fourth moments of the nuclear resonance line in the vicinity of ω_0 due to nuclear dipolar and exchange interactions by a diagonal sum method. Only contributions due to the resonance line centered at ω_0 were considered. In the case of only a single kind of magnetic nuclei with gyromagnetic ratio γ and spin I the second moment M_2 in units of (rad sec^{-1})^2, is as follows:

$$\frac{I(I+1)}{3N\hbar^2}\sum_{j\neq k} b_{jk}^2, \qquad (2)$$

where

$$b_{jk}=(3\gamma^2\hbar^2/2r_{jk}^3)(1-3\cos^2\theta_{jk}).$$

N is the total number of nuclei in the crystal, $\mathbf{r}_{jk}$ is the radius vector between nuclei j and k, and θ_{jk} is the angle between the direction of the applied static magnetic field and the vector $\mathbf{r}_{jk}$.

The fourth moment M_4 in the absence of exchange interactions is as follows[1]:

$$M_4=\Big[3\Big(N^{-1}\sum_{j\neq k} b_{jk}^2\Big)^2-(\tfrac{1}{3})N^{-1}\sum_{jkl\neq} b_{jk}^2(b_{jl}-b_{kl})^2$$
$$-(\tfrac{1}{5})N^{-1}\sum_{k\neq j} b_{jk}^4\{8+(\tfrac{3}{2})(I^2+I)^{-1}\}\Big]\left\{\frac{I(I+1)}{3\hbar^2}\right\}^2. \qquad (3)$$

The evaluation of M_2 requires a summation over pairs of nuclei. M_4 consists of three types of terms: (1) terms containing the quantity b_{jk} to the fourth power, (2) terms which are proportional to the square of M_2, and (3) terms which involve a summation over all possible triangles formed by triplets of nuclei.

In the more general case of two species of spins with exchange interactions between them, the corresponding expressions for M_2 and M_4 are somewhat more complicated[1]; however, as will be evident from the discussion in the following sections these situations yield the same kind of irreducible forms as do the simpler expressions given in Eqs. (2) and (3). In the following two sections we shall further limit the discussion without loss of generality to only one magnetic nucleus per unit cell. In Sec. V the effects of space group symmetry and other magnetic nuclear species will be examined.

III. COORDINATE TRANSFORMATIONS OF M_2

To put the expression for the second moment M_2 in its most convenient form we will rewrite M_2 in a coordinate system fixed in the crystal. In order to accomplish this, b_{jk} will be expressed as a spherical harmonic; thus we will write

$$b_{jk}=-3(4\pi/5)^{1/2}\gamma^2\hbar^2 Y_{20}(jk)r_{jk}^{-3},$$

where jk, the argument of Y_{20}, refers to the angle θ_{jk} between the applied field $\mathbf{H}$ and the radius vector $\mathbf{r}_{jk}$. M_2 will contain $Y_{20}(jk)$ squared which by the coupling rule for spherical harmonics[7] may be expressed as a sum of spherical harmonics of orders 0, 2, and 4 as follows:

$$Y_{20}(jk)Y_{20}(jk)=\frac{5}{(4\pi)^{1/2}}\sum_{L=0,2,4}\frac{C(22L;00)^2}{(2L+1)^{1/2}}Y_{L0}(jk), \qquad (4)$$

and hence from Eq. (2)

$$M_2=3(4\pi)^{1/2}\gamma^4\hbar^2 I(I+1)\sum_k\sum_L\frac{C(22L;00)^2}{(2L+1)^{1/2}}\frac{Y_{L0}(jk)}{r_{jk}^6}, \qquad (5)$$

where the quantity $C(22L;00)$ is a Clebsch-Gordan coefficient[7] which has the general form $C(l_1,l_2,l;m_1,m-m_1)$; the projection quantum numbers satisfy $m_1+m_2=m$ while the numbers l_1, l_2, and l form a triangle with $|l_1-l_2|\leqslant l\leqslant|l_1+l_2|$.

It is not clear from this form of M_2 how M_2 depends on the orientation of the applied field $\mathbf{H}$ relative to axes fixed in the crystal, which is what can be ascertained in an experiment. To remedy this we transform the $Y_{L0}(jk)$ from the laboratory coordinate system whose z axis is along $\mathbf{H}$ to the crystal coordinate system. This may be performed by means of the spherical harmonic addition theorem[7] by which a spherical harmonic ($m=0$) with coordinates θ_{jk}, ϕ_{jk} is expressed in terms of the polar coordinates θ, ϕ of $\mathbf{H}$ relative to the crystal coordinate system and the polar coordinates $\bar{\theta}_{jk}$, $\bar{\phi}_{jk}$ of the vector $\mathbf{r}_{jk}$ relative to the crystal coordinate system as shown in Fig. 1. M_2 now takes on the

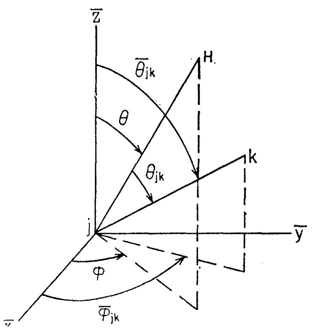

FIG. 1. Coordinates associated with transformation between laboratory (H) and crystal ($\bar{x},\bar{y},\bar{z}$) coordinate systems.

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[7] Our notations for spherical harmonics and Clebsch-Gordan coefficients will follow those of M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

following form:

$$M_2=12\pi\gamma^4\hbar^2I(I+1)\sum_k\sum_L\sum_M\frac{C(22L;00)^2}{2L+1}\times\frac{Y_{LM}^*(\bar{j}\bar{k})}{r_{jk}^6}Y_{LM}(\theta,\phi),\tag{6}$$

where M runs from $-L$ to L and $\bar{j}\bar{k}$ refers to the orientation of $\mathbf{r}_{jk}$ relative to the crystal coordinate system. M_2 is now in the form of a finite series of

$$\sum_{L=0,2,4}(2L+1)=15$$

spherical harmonics. The Y_{LM} are a complete and orthonormal set of functions but are also generally somewhat redundant since the coefficients of these functions, i.e., the lattice sums, are generally not all independent due to restrictions imposed by the symmetry of the crystal. To determine the number of independent parameters it is necessary to rewrite M_2 in terms of lattice harmonics of the crystal.

The lattice harmonics $X_L^{\mu\alpha i}$ form a basis for an irreducible representation μ of the crystal point group.[5,6] $\mu=1$ will always be used for the identity representation. α labels different sets of functions belonging to the same representation μ; i labels the different basis functions within a representation μ, α. That is, if R is an element of the point group G, then[8]

$$P_RX_L^{\mu\alpha i}=\textstyle\sum_j D^{(\mu)}(R)_{ji}X_L^{\mu\alpha j},\tag{7}$$

where P_R is a unitary operator defined by Wigner[8] and $D^{\mu}(R)_{ji}$ is a matrix element of the μth irreducible matrix representation of the Group G. The $X_L^{\mu\alpha i}$ may be derived from spherical harmonics of order L by a unitary transformation.

$$\begin{aligned}X_L^{\mu\alpha i}&=\sum_M U_{\mu\alpha i,M}{}^LY_{LM},\\ Y_{LM}&=\sum_{\mu\alpha i}U_{\mu\alpha i,M}{}^{L*}X_L^{\mu\alpha i},\end{aligned}\tag{8}$$

where the sum on M runs from $-L$ to L. Since the $(2L+1)\times(2L+1)$ transformation matrix $\mathbf{U}^L$ is unitary, the $X_L^{\mu\alpha i}$ also constitute a complete and orthonormal set of functions. Using the unitary properties of the transformation of Eq. (8), one finds upon substitution of the Y_{LM} for $X_L^{\mu\alpha i}$ in Eq. (6) that

$$M_2=12\pi\gamma^4\hbar^2I(I+1)\sum_k\sum_{L\mu\alpha i}\frac{[C(22L;00)]^2}{2L+1}\times\frac{X_L^{\mu\alpha i*}(\bar{j}\bar{k})}{r_{jk}^6}X_L^{\mu\alpha i}(\theta,\phi).\tag{9}$$

However, the coefficients of only those lattice harmonics $X_L^{1\alpha}$ (θ,ϕ) which belong to the identity $(\mu=1)$ representation are different from zero. This is necessary since, as is physically evident, M_2 must be invariant under all the operations of the point group G. A more formal proof is as follows. M_2 may be expressed as a linear combination of lattice harmonics:

$$M_2(\theta,\phi)=\sum_L\sum_{\mu\alpha i}C_L^{\mu\alpha i}X_L^{\mu\alpha i}(\theta,\phi),\tag{10}$$

where $C_L^{\mu\alpha i}$ are coefficients and (θ,ϕ) refer to the orientation of the crystal relative to a particular set of laboratory coordinate axes. Since M_2 is invariant under any rotation R which belongs to the point group G, it follows that:

$$\begin{aligned}M_2(\theta,\phi)&=\frac{1}{g}\sum_{\mathrm{R}\in\mathrm{g}}P_RM_2\\ &=\sum_{\mathrm{R}\in\mathrm{g}}\sum_L\sum_{\mu\alpha ii'}\frac{1}{g}C_L^{\mu\alpha i}D^{(\mu)}(R)_{i'i}X_L^{\mu\alpha i'}\\ &=\sum_L\sum_{\mu\alpha i}C_L^{\mu\alpha i}\delta_{\mu 1}\delta_{i'i}X_L^{\mu\alpha i'}=\sum_{L\alpha}C_L^{1\alpha}X_L^{1\alpha},\end{aligned}\tag{11}$$

where g is the order of the group G, $P_RM_2=M_2(\theta',\phi')$, (θ',ϕ') being the orientation of the crystal after the application of the symmetry operation R. The last step follows from the orthogonality relation of the irreducible representations.[8]

Since only coefficients of lattice harmonics belonging to the identity representation may be different from zero for M_2, (9) may be simplified to

$$\begin{aligned}M_2&=12\pi\gamma^4\hbar^2I(I+1)\sum_k\sum_{L,\alpha}\frac{[C(22L;00)]^2}{2L+1}\times\frac{X_L^{1\alpha*}(\bar{j}\bar{k})}{r_{jk}^6}X_L^{1\alpha}(\theta,\phi)\\ &=\frac{12\pi}{5}\gamma^4\hbar^2I(I+1)\sum_k\Bigg[\frac{X_0^{1*}(\bar{j}\bar{k})}{r_{jk}^6}X_0^1(\theta,\phi)\\ &\quad+(2/7)\sum_\alpha\frac{X_2^{1\alpha*}(\bar{j}\bar{k})}{r_{jk}^6}X_2^{1\alpha}(\theta,\phi)\\ &\quad+(2/7)\sum_\alpha\frac{X_4^{1\alpha*}(\bar{j}\bar{k})}{r_{jk}^6}X_4^{1\alpha}(\theta,\phi)\Bigg],\end{aligned}\tag{12}$$

$X_0^1(\theta,\phi)=(4\pi)^{-1/2}$.

The number of independent parameters needed to specify M_2 is obviously equal to the total number of lattice harmonics $N_2(G)$ which belong to the identity representation for $L=0$, 2, and 4. This quantity $N_2(G)$ may be seen to be equal to the total number of times the identity representation of the point group G occurs in the direct sum decomposition of the representation

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[8] E. P. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959), Chaps. 9 and 11.

TABLE I. Number of independent components for second and fourth moments [$N_2(G)$ and $N_4(G)$].

System	Point group G	Number of times that the identity representation occurs $L=0$	$L=2$	$L=4$	$L=6$	$L=8$	$N_2(G)$	$N_4(G)$
Triclinic	C_1	1	5	9	13	17	15	45
	C_i	1	5	9	13	17	15	45
Monoclinic	C_2	1	3	5	7	9	9	25
	C_s	1	3	5	7	9	9	25
	C_{2h}	1	3	5	7	9	9	25
Orthorhombic	D_2	1	2	3	4	5	6	15
	C_{2v}	1	2	3	4	5	6	15
	D_{2h}	1	2	3	4	5	6	15
Trigonal	C_3	1	1	3	5	5	5	15
	C_{3i}	1	1	3	5	5	5	15
	D_3	1	1	2	3	3	4	10
	C_{3v}	1	1	2	3	3	4	10
	D_{3d}	1	1	2	3	3	4	10
Tetragonal	C_4	1	1	3	3	5	5	13
	S_4	1	1	3	3	5	5	13
	C_{4h}	1	1	3	3	5	5	13
	D_4	1	1	2	2	3	4	9
	C_{4v}	1	1	2	2	3	4	9
	D_{2d}	1	1	2	2	3	4	9
	D_{4h}	1	1	2	2	3	4	9
Hexagonal	C_6	1	1	1	3	3	3	9
	C_{3h}	1	1	1	3	3	3	9
	C_{6h}	1	1	1	3	3	3	9
	D_6	1	1	1	2	2	3	7
	C_{6v}	1	1	1	2	2	3	7
	D_{3h}	1	1	1	2	2	3	7
	D_{6h}	1	1	1	2	2	3	7
Cubic	T	1	0	1	2	1	2	5
	T_h	1	0	1	2	1	2	5
	O	1	0	1	1	1	2	4
	T_d	1	0	1	1	1	2	4
	O_h	1	0	1	1	1	2	4

of the full rotation group for $L=0$, 2, and 4. We denote the representations of the full rotation group by Γ_L and those of the point group G by Δ_μ. Then

$$\Gamma_L=\sum_\mu a_{\mu L}\Delta_\mu, \tag{13}$$

where the $a_{\mu L}$ are integers. Therefore,

$$N_2(G)=\sum_{L=0,2,4} a_{1L} \tag{14}$$

is the total number of times the identity representation occurs in M_2. The quantities a_{1L} are determined as follows:

$$a_{1L}=(1/g)\sum_{i=1}^{r} r_i\chi_i^L, \tag{15}$$

where g is the order of the group, r_i is the number of elements contained in the ith class, χ_i^L is the character of the representation L for the ith class, and r is the total number of classes. χ_i^L is equal to $\sin[(L+\frac{1}{2})\phi_i]/\sin(\phi_i/2)$ where ϕ_i is the rotation angle corresponding to the operations of the ith class. The quantities $N_2(G)$ determined in this manner for all 32 point groups are given in Table I. $N_2(G)$ ranges from 15 for triclinic C_1 symmetry to 2 for cubic O_h symmetry. Only the *eleven* proper (Laue) point groups are distinguished by $N_2(G)$ due to the occurrence of only even values of L in M_2. Only even values of L occur since M_2 has even parity with respect to reversal of the direction of the applied field $\mathbf{H}$. As a result, nuclear magnetic resonance measurements cannot distinguish between proper and improper point groups which differ only by the inclusion of the inversion operator or an improper rotation for the corresponding proper rotation. However, as will be discussed in Sec. VII, the application of external electric field to the crystal may allow such a distinction.

M_2 in the form of Eq. (12) is most useful in the analysis of experimental data. The lattice harmonics corresponding to various point groups have been tabulated by Bell.[6] These functions may be also generated by the idempotent method.[9] Since nuclear magnetic resonance moment data are usually obtained by rotation of the crystal about an axis perpendicular to the field $\mathbf{H}$, it is useful to project the $X_{1\alpha}{}^L(\theta,\phi)$ into such a plane. This always yields the angular dependence of M_2 in the form of a finite series in $e^{\pm im\psi}$ $(m\leq 4)$ where ψ is the angle of rotation. A similar angular dependence has been demonstrated by McCall and Hamming.[10] This procedure will be further illustrated in Sec. VI.

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[9] J. S. Lomont, *Applications of Finite Groups* (Academic Press Inc., New York, 1959), Chap. III, Sec. 9.

[10] D. W. McCall and R. W. Hamming, Acta. Cryst. **12**, 81 (1959).

IV. FOURTH MOMENT

The various sums which occur in the expression for the fourth moment of Eq. (3) may be classified into three distinct types of terms in increasing order of complexity.

$$\text{Type I:}\quad \textstyle\sum_k b_{jk}^4,$$

$$\text{Type II:}\quad (\textstyle\sum_k b_{jk}^2)^2,$$

$$\text{Type III:}\quad \sum_{k\neq n} b_{jk}^2 b_{jn} b_{kn}.$$

In analogy with the treatment of the second moment given above, we wish to express the fourth moment as a series of lattice harmonics in the crystal coordinate system. In the following each type of term is considered in the order given above.

Type I

By repeated application of the coupling rule for spherical harmonics one finds

$$[Y_{20}(jk)]^4=\frac{25}{(4\pi)^{\frac{3}{2}}}\sum_L\left[\sum_{ll'}C(22l;00)^2C(22l';00)^2\times\frac{C(ll'L;00)^2}{(2L+1)^{1/2}}\right]Y_{L0}(jk),\quad(16)$$

where l, $l'=0$, 2, 4 and $L=0$, 2, 4, 6, 8. Once again one may transform $Y_{L0}(jk)$ to the crystal coordinate system and express $\sum b_{jk}^4$ in terms of lattice harmonics belonging to the identity representation. The result is as follows:

$$\sum_k b_{jk}^4=(3\gamma^2\hbar^2)^4\sum_{L\alpha}\sum_{ll'}\sum_k C(22l;00)^2C(22l';00)^2\times\frac{C(ll'L;00)^2}{\beta_L^2}\frac{X_L^{1\alpha *}(\bar{j}\bar{k})}{r_{jk}^{12}}X_L^{1\alpha}(\theta,\phi),$$

where $\beta_L=[(2L+1)/4\pi]^{1/2}$, summation is over $L=0$, 2, 4, 6, 8. For simplicity let

$$\frac{4\pi}{2L+1}\sum_{ll'}C(22l;00)^2C(22l';00)^2C(ll'L;00)^2=A_L,$$

hence

$$\sum b_{jk}^4=(3\gamma^2\hbar^2)^4\sum_k\sum_{L\alpha}A_L\frac{X_L^{1\alpha *}(\bar{j}\bar{k})}{r_{jk}^{12}}X_L^{1\alpha}(\theta,\phi),\quad(17)$$

where

$$A_0=12\pi/35,\quad A_2=16\pi/77,\quad A_4=816\pi/5005,$$
$$A_6=288\pi/5005,\quad A_8=288\pi/12155.$$

Type II

Since these terms are proportional to the square of M_2, we may evaluate them directly from Eq. (12). In doing so we obtain products of identity representation lattice harmonics. These, in close analogy to the coupling rule for spherical harmonics may be expressed as a linear combination of lattice harmonics belonging to the identity representation, as is discussed more fully in Appendix A.

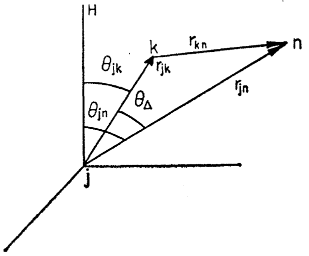

FIG. 2. Orientation of the triangle *jkn* in the laboratory coordinate system.

$$X_{L_1}^{1\alpha_1}(\theta,\phi)X_{L_2}^{1\alpha_2 *}(\theta,\phi)=\sum_{L\alpha}\langle L_1(1\alpha_1)L_2(1\alpha_2)|L\alpha\rangle X_L^{1\alpha}(\theta,\phi),\quad(18)$$

where $\langle L_1(1\alpha_1)L_2(1\alpha_2)|L\alpha\rangle$ is a coupling coefficient for lattice harmonics analogous to the Clebsch-Gordan coefficients.

Using Eq. (18) one finds

$$(\sum_k b_{jk}^2)^2=(3\gamma^2\hbar^2)^4\sum_{L\alpha}\left\{\sum_{kn}\sum_{L_1\alpha_1}\sum_{L_2\alpha_2}\langle L_1(1\alpha_1)L_2(1\alpha_2)|L\alpha\rangle\times\frac{C(22L_1;00)^2}{\beta_{L_1}^2}\frac{C(22L_2;00)^2}{\beta_{L_2}^2}\frac{X_{L_1}^{1\alpha_1 *}(\bar{j}\bar{k})}{r_{jk}^6}\times\frac{X_{L_2}^{1\alpha_2}(\bar{j}\bar{n})}{r_{jn}^6}\right\}X_L^{1\alpha}(\theta,\phi),\quad(19)$$

where L takes on the values 0, 2, 4, 6, 8.

Type III

Terms of this type require considerably more manipulation to place into the desired form than that required for terms of types I and II. This is the case since terms of type III involve a summation over all possible triangles formed by triplets of nuclei *jkn* where *j*, *k*, or *n* are not equal to each other. It will be convenient to express b_{kn} in terms of b_{jk} and b_{jn}. Referring to Fig. 2 (which is drawn in the magnetic field coordinate system), $Y_{20}(kn)$ may be expressed in terms of θ_{jk}, θ_{jn}, and θ_Δ, where θ_Δ is the angle between the vectors $\mathbf{r}_{jk}$ and $\mathbf{r}_{jn}$. Noting that

$$\cos\theta_{kn}=(r_{jn}/r_{kn})\cos\theta_{jn}-(r_{jk}/r_{kn})\cos\theta_{jk},$$

and $r_{kn}^2=r_{jk}^2+r_{jn}^2-2r_{jk}r_{jn}\cos\theta_\Delta$, it follows that

$$Y_{20}(kn)=(r_{jn}^2/r_{kn}^2)Y_{20}(jn)+(r_{jk}^2/r_{kn}^2)Y_{20}(jk)-(5\times4\pi)^{1/2}(r_{jk}r_{jn}/r_{kn}^2)Y_{10}(jn)Y_{10}(jk)+(5/4\pi)^{1/2}(r_{jk}r_{jn}/r_{kn}^2)\cos\theta_\Delta.\quad(20)$$

By means of Eq. (20) one may express b_{kn} as a sum of four terms, each of which, when incorporated into $\sum b_{jk}{}^2 b_{jn} b_{kn}$, gives rise to a sum which may be reduced to the standard form, i.e., a sum of lattice harmonics of the identity representation in the crystal coordinate system. The techniques involved in this procedure will be illustrated for the sum arising from the first term on the right side of Eq. (20) which we designate by $(\sum_{k\neq n} b_{jk}{}^2 b_{jn} b_{kn})_a$:

$$\Big(\sum_{k\neq n} b_{jk}{}^2 b_{jn} b_{kn}\Big)_a = (3\gamma^2\hbar^2)^4 \sum_{k\neq n}\sum_{ll'} \frac{C(22l;00)^2}{\beta_l}\frac{C(22l';00)^2}{\beta_{l'}} \times \frac{Y_{l0}(jk)Y_{l'0}(jn)}{r_{jk}{}^6 r_{jn} r_{kn}{}^5}.$$

Transforming to the crystal coordinate system, using the coupling rule for spherical harmonics $Y_{lm}(\theta,\phi)$ and $Y_{l'm'}(\theta,\phi)$ and proceeding to lattice harmonics through the transformation of Eq. (8) one obtains

$$\Big(\sum_{k\neq n} b_{jk}{}^2 b_{jn} b_{kn}\Big)_a = (3\gamma^2\hbar^2)^4 \Big(\frac{4\pi}{5}\Big)^2 \sum_{ll'}\sum_{mm'}\sum_{\mu'\alpha'i'}\sum_{\mu\alpha i}\sum_{LA} \frac{\beta_2{}^4\beta_L}{\beta_l{}^3\beta_{l'}}$$
$$\times C(22l;00)^2 C(22l';00)^2 C(l'Ll;00)$$
$$\times C(l'Ll;m',m-m')U_{\mu\alpha i m}{}^{l} U_{\mu'\alpha'i'm'}{}^{l'*} U_{1A,m-m'}{}^{L*}$$
$$\times\Bigg[\sum_{k\neq n} \frac{X_l{}^{\mu\alpha i*}(\bar{j}\bar{k}) X_{l'}{}^{\mu'\alpha'i'}(\bar{j}\bar{n})}{r_{jk}{}^6 r_{jn} r_{kn}{}^5}\Bigg] X_L{}^{1A}(\theta,\phi), \quad (21)$$

where $L=0$, 2, 4, 6, 8. Since $(\sum_{k\neq n} b_{jk}{}^2 b_{jn} b_{kn})_a$ is invariant when the static magnetic field direction is rotated by an operation of the point group G, only $X_L{}^{\mu\alpha i}(\theta,\phi)$ which belong to the identity representation can occur. (See proof given in Sec. III.)

A simplication of Eq. (21) may be made by consideration of the effect of operations of the point group of the crystal on the quantity enclosed in brackets in Eq. (21). It may be shown that

$$\sum_{k\neq n} \frac{X_l{}^{\mu\alpha i*}(\bar{j}\bar{k}) X_{l'}{}^{\mu'\alpha'i'}(\bar{j}\bar{n})}{r_{jk}{}^6 r_{jn} r_{kn}{}^5} \equiv \delta_{ii'}\delta_{\mu\mu'} \sum_{\Delta}\frac{n_\Delta}{d_\mu}\sum_p \frac{X_l{}^{\mu\alpha p*}(\bar{j}\bar{k}) X_{l'}{}^{\mu\alpha' p}(\bar{j}\bar{n})}{r_{jk}{}^6 r_{jn} r_{kn}{}^5}, \quad (22)$$

where $\sum_\Delta$ indicates a sum over all inequivalent triangles, i.e., triangles that cannot be brought into coincidence by an operation of the point group, n_Δ is the number of equivalent triangles formed by a triplet jkn, (that is, n_Δ is the number of distinct triangles that may be obtained by applying all operations of the point group to the triangle jkn) and d_μ is the dimensionality of the μth irreducible representation of G. On the right side of (22), $\bar{j}\bar{k}$ and $\bar{j}\bar{n}$ refers to the orientation of two sides jk and jn of a particular triangle.

The proof is as follows. Once again we make use of the orthogonality relations between irreducible representations of G. Operate on $r_{jk}{}^{-6} r_{jn}{}^{-1} r_{kn}{}^{-5} X_l{}^{\mu\alpha i*}(\bar{j}\bar{k}) \times X_{l'}{}^{\mu'\alpha'i'}(\bar{j}\bar{n})$ (where $\bar{j}\bar{k}$ and $\bar{j}\bar{n}$ are the orientation of two sides jk and jn of a particular triangle) with an element R of G and sum over R. Since the distances r_{jn}, etc., are invariant under R, only the effect on the lattice harmonics will be indicated.

$$\sum_R P_R X_l{}^{\mu\alpha i*}(jk) P_R X_l{}^{\mu'\alpha'i'}(\bar{j}\bar{n})$$
$$= \sum_R \sum_{pp'} D^{(\mu)}(R)_{pi}{}^* D^{(\mu')}(R)_{p'i'} X_l{}^{\mu\alpha p*}(\bar{j}\bar{k}) X_{l'}{}^{\mu'\alpha'p'}(\bar{j}\bar{n})$$
$$= d_\mu{}^{-1} g \sum_{pp'} \delta_{\mu\mu'}\delta_{ii'}\delta_{pp'} X_l{}^{\mu\alpha p*}(\bar{j}\bar{k}) X_{l'}{}^{\mu'\alpha'p'}(\bar{j}\bar{n})$$
$$= d_\mu{}^{-1} g \delta_{\mu\mu'}\delta_{ii'} \sum_p X_l{}^{\mu\alpha p*}(\bar{j}\bar{k}) X_{l'}{}^{\mu\alpha' p}(\bar{j}\bar{n}).$$

Also, we have

$$\sum_R P_R X_l{}^{\mu\alpha i*}(\bar{j}\bar{k}) P_R X_{l'}{}^{\mu'\alpha'i'}(\bar{j}\bar{n}) = g n_\Delta{}^{-1} \sum X_l{}^{\mu\alpha i*}(\bar{j}\bar{k}) X_{l'}{}^{\mu'\alpha'i'}(\bar{j}\bar{n}),$$

where the summation on the right side of the above equation is carried over all distinct triangles that may be generated from the particular jkn triangle by applying all rotation operations of the point Group G. Therefore Eq. (22) follows. Using (22), (21) may be simplified to the following:

$$\Big(\sum_{k\neq n} b_{jk}{}^2 b_{jn} b_{kn}\Big)_a = (3\gamma^2\hbar^2)^4 \sum_{\mu,\alpha,\alpha',i,m,m'} \beta_l{}^{-3}\beta_{l'}{}^{-1}\beta_L$$
$$\times C(22l;00)^2 C(22l',00)^2 C(l'Ll;00) C(l'Ll;m',m-m')$$
$$\times U_{\mu\alpha i m}{}^{l} U_{\mu\alpha' i m'}{}^{l'*} U_{1A,m-m'}{}^{L*} \Big\{\sum_\Delta n_\Delta d_\mu{}^{-1} \sum_p r_{jk}{}^{-6} r_{jn}{}^{-1}$$
$$\times r_{kn}{}^{-5} X_l{}^{\mu\alpha p*}(\bar{j}\bar{k}) X_{l'}{}^{\mu\alpha' p}(\bar{j}\bar{n})\Big\} X_L{}^{1A}(\theta,\phi).$$

This equation may be further simplified by noting that

$$\langle l(\mu\alpha)l'(\mu\alpha')|LA\rangle \equiv \beta_l{}^{-1}\beta_{l'}\beta_L \sum_{m,m',i} U_{\mu\alpha i m}{}^{l} U_{\mu\alpha' i m'}{}^{l'*} U_{1A,m-m'}{}^{L*}$$
$$\times C(l'Ll;m'm-m')C(l'Ll;00), \quad (23)$$

where $\langle l(\mu\alpha)l'(\mu\alpha')|LA\rangle$ is the coupling coefficient for lattice harmonics. A discussion of these coupling coefficients may be found in Appendix A.

Using (23), we get

$$\Big(\sum_{k\neq n} b_{jk}{}^2 b_{jn} b_{kn}\Big)_a = (3\gamma^2\hbar^2)^4 \sum_{LA} \Bigg\{\sum_{ll'} C(22l;00)^2 \times\frac{C(22l';00)^2}{\beta_l{}^2\beta_{l'}{}^2} \sum_{\mu\alpha\alpha'} (\langle l(\mu\alpha),l'(\mu\alpha')|LA\rangle)$$
$$\times \sum_\Delta \frac{n_\Delta}{d_\mu} \sum_p \frac{X_l{}^{\mu\alpha p*}(\bar{j}\bar{k}) X_{l'}{}^{\mu\alpha' p}(\bar{j}\bar{n})}{r_{jk}{}^6 r_{jn} r_{kn}{}^5}\Bigg\} X_L{}^{1A}(\theta,\phi). \quad (24a)$$

The remaining three contributions to $\sum b_{jk}^2 b_{jn} b_{kn}$ arising from Eq. (20) may be evaluated by similar procedures. The final results for type III terms is as follows where the remaining terms of Eq. (20) are labeled by b, c, and d

$$\Big(\sum_{k\neq n} b_{jk}^2 b_{jn} b_{jn}\Big)_b = (3\gamma^2\hbar^2)^4 \sum_{LA} \Bigg\{ \sum_{ll'} C(22l;00)^2 \frac{C(l2l';00)^2}{\beta_2^2\beta_{l'}^2} \sum_{\mu\alpha\alpha'} (\langle l(\mu\alpha),2(\mu\alpha')|LA\rangle) \times \sum_{\Delta} \frac{n_\Delta}{d_\mu} \sum_{p} \frac{X_{l'}^{\mu\alpha p*}(\bar{j}\bar{k}) X_2^{\mu\alpha' p}(\bar{j}\bar{n})}{r_{jk}^4 r_{jn}^3 r_{kn}^5} \Bigg\} X_L^{1A}(\theta,\phi) \quad (24b)$$

$$\Big(\sum_{k\neq n} b_{jk}^2 b_{jn} b_{kn}\Big)_c = -3(3\gamma^2\hbar^2)^4 \sum_{LA} \Bigg\{ \sum_{ll_1l_2} C(22l;00)^2 \frac{C(l1l_1;00)^2 C(21l_2;00)^2}{\beta_{l_1}^2\beta_{l_2}^2} \sum_{\mu\alpha\alpha'} (\langle l_1(\mu\alpha),l_2(\mu\alpha)|LA\rangle) \times \sum_{\Delta} \frac{n_\Delta}{d_\mu} \sum_{p} \frac{X_{l_1}^{\mu\alpha p*}(\bar{j}\bar{k}) X_{l_2}^{\mu\alpha' p}(\bar{j}\bar{n})}{r_{jk}^5 r_{jn}^2 r_{kn}^5} \Bigg\} X_L^{1A}(\theta,\phi) \quad (24c)$$

$$\Big(\sum_{k\neq n} b_{jk}^2 b_{jn} b_{kn}\Big)_d = (3\gamma^2\hbar^2)^4 \sum_{LA} \Bigg\{ \sum_{l} \frac{C(22l;00)^2}{\beta_l^2\beta_2^2} \sum_{\mu\alpha\alpha'} (\langle l(\mu\alpha),2(\mu\alpha')|LA\rangle) \times \sum_{\Delta} \frac{n_\Delta}{d_\mu} \sum_{p} \frac{X_{l}^{\mu\alpha p*}(\bar{j}\bar{k}) X_2^{\mu\alpha' p}(\bar{j}\bar{n}) \cos\theta_\Delta}{r_{jk}^5 r_{jn}^2 r_{kn}^5} \Bigg\} X_L^{1A}(\theta,\phi). \quad (24d)$$

The total of type III terms is simply the sum of the above contributions IIIa, IIIb, IIIc, and IIId. In all of the above expressions $L=0$, 2, 4, 6 or 8. Values of the l values for other terms are as follows:

Type IIIa: l, $l'=0$, 2, 4.

Type IIIb: $l=0$, 2, 4; $l'=0$, 2, 4, 6.

Type IIIc: $l=0$, 2, 4; $l_1=1$, 3, 5; $l_2=1$, 3.

Type IIId: $l=0$, 2, 4.

The values which the various l's may assume for a nonzero result are determined by the symmetry properties of the Clebsch-Gordan coefficients.[7] Values of these coefficients that are necessary in the evaluation of M_2 and M_4 are tabulated in Table II as calculated from standard formulas.[7] The vector coupling coefficients for lattice harmonics may be calculated by a method discussed in Appendix A. Values of the quantities $\langle l(\mu\alpha),l'(\mu\alpha'),|LA\rangle$ for cubic O_h symmetry are given in Table III.

The number of independent components $N_4(G)$ needed to determine the fourth moment may be determined by precisely the same method used for the second moment; that is, $N_4(G)$ is the number of times the identity representation of G occurs in the direct sum decomposition of the representations of the full rotation group for $L=0$, 2, 4, 6, and 8. $N_4(G)$ have been determined for all 32 point groups and are given in Table I.

By means of the above expressions the second and fourth moments may be readily written down as a finite series of lattice harmonics in the coordinate system of the crystal. Before illustrating the method in Sec. VI, aspects pertinent to the choice of a crystal coordinate system and the effect of space group symmetry will be discussed.

V. SPACE GROUP SYMMETRY

The space group of a crystal is the entire group of operations which leaves the crystal invariant.[11] The space group ($\mathcal{G}$) may be expressed as the direct product of two subgroups: the translation group of the lattice (T) and a group of operations (S) which is simply isomorphic to the point group of the crystal. The effect of an element of (T) on a radius vector $\mathbf{r}$ may be represented as follows

$$T_{n_1n_2n_3}\mathbf{r} = \mathbf{r} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3,$$

where n_1, n_2, and n_3 are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are unit lattice vectors. The effect of an element of (S) on

TABLE II. Clebsch-Gordan coefficients $C(l_1l_2L;00)$.

l_1	l_2	L	$C(l_1l_2L;00)$
0	0	0	1
2	2	0	$5^{-1/2}$
4	4	0	1/3
1	0	1	1
2	1	1	$-(2/5)^{1/2}$
2	0	2	1
2	2	2	$-(2/7)^{1/2}$
4	2	2	$(2/7)^{1/2}$
4	4	2	$-(5/3)(4/77)^{1/2}$
2	1	3	$(3/5)^{1/2}$
4	1	3	$-2/3$
2	2	4	$(18/35)^{1/2}$
4	2	4	$-(20/77)^{1/2}$
4	4	4	$9(2/1001)^{1/2}$
4	1	5	$(5/9)^{1/2}$
4	2	6	$(5/11)^{1/2}$
4	4	6	$-(2/3)(5/11)^{1/2}$
4	4	8	$(7/3)(10/143)^{1/2}$

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[11] For a general discussion, see W. H. Zachariasen, *Theory of X-Ray Diffraction in Crystals* (John Wiley & Sons, Inc., New York, 1945).

TABLE III. Tabulation of $(4\pi)^{1/2}\langle l(\mu\alpha),l'(\mu\alpha')|LA\rangle$ for cubic group O_h.[a]

l	l'	μ	$L=0$	$L=4$	$L=6$	$L=8$
1	1	$10(p)$	3			
1	3	$10(p)$	0	2		
1	5	$10_1(p_1)$	0	$\frac{5}{2}(7/11)^{1/2}$	$9(3/286)^{1/2}$	
1	5	$10_2(p_2)$	0	$\frac{3}{2}(5/11)^{1/2}$	$-3(105/286)^{1/2}$	
2	2	$3(d)$	2	$(12/7)^{1/2}$		
2	2	$4(d')$	3	$-(12/7)^{1/2}$		
2	4	$3(d)$	0	$40(7)^{1/2}/77$	$(15/11)(6/13)^{1/2}$	
2	4	$4(d')$	0	$-30(7)^{1/2}/77$	$(60/11)(3/26)^{1/2}$	
2	6	$3(d)$	0	$(10/11)(30/13)^{1/2}$	$(4/11)(7/5)^{1/2}$	$2(462/1105)^{1/2}$
2	6	$4_1(d_1')$	0	$(5/22)(39/2)^{1/2}$	$-15(7)^{1/2}/22$	0
2	6	$4_2(d_2')$	0	$(15/2)(15/286)^{1/2}$	$(3/2)(7/55)^{1/2}$	$-8(42/1105)^{1/2}$
3	3	$7(f)$	1	$-2(21)^{1/2}/33$	$(20/11)(2/13)^{1/2}$	
3	3	$10(p)$	3	$3(21)^{1/2}/11$	$(25/11)(2/13)^{1/2}$	
3	3	$9(f')$	3	$-(21)^{1/2}/11$	$-(45/11)(2/13)^{1/2}$	
3	5	$10_1(p_1)$	0	$(30/13)(3/11)^{1/2}$	$(7/2)(7/286)^{1/2}$	$(21/13)(21/17)^{1/2}$
3	5	$10_2(p_2)$	0	$-(6/13)(105/11)^{1/2}$	$(21/2)(5/286)^{1/2}$	$(7/13)(15/17)^{1/2}$
3	5	$9(f')$	0	$-(10/13)(21/11)^{1/2}$	$-21(286)^{-1/2}$	$(42/13)(3/17)^{1/2}$
4	4	$1(s)$	1	$18(21)^{1/2}/143$	$(20/11)(2/13)^{1/2}$	$(70/13)(3/187)^{1/2}$
4	4	$3(d)$	2	$(36/143)(3/7)^{1/2}$	$-(32/11)(2/13)^{1/2}$	$(98/13)(3/187)^{1/2}$
4	4	$5(g)$	3	$27(21)^{1/2}/143$	$-(3/11)(2/13)^{1/2}$	$(168/13)(3/187)^{1/2}$
4	4	$4(d')$	3	$-(27/11)(3/7)^{1/2}$	$(15/11)(2/13)^{1/2}$	0

[a] The blank spaces in this table correspond to the case l, l', L do not form a triangle; hence the coefficients always vanish. The representations μ in Bell's notation are given in parentheses. The letters α and A are always omitted because there is only one representation. The letter α' is written as a subscript for μ in cases where there is more than one μth representation for l'.

a radius vector **r** may be given by

$$\begin{aligned} S\cdot\mathbf{r} &= [\mathbf{R},\mathbf{t}]\cdot\mathbf{r} \\ &= \mathbf{R}\cdot\mathbf{r}+\mathbf{t}, \end{aligned}$$

where $\mathbf{R}$ is a dyadic representing a proper or improper rotation and if not the null vector, $\mathbf{t}$ is a nonprimitive translation, i.e., $\mathbf{t}$ cannot be expressed as a lattice vector of the form $n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$. (T) must be an invariant subgroup of the space group. This results in the requirement that the elements of $\mathbf{R}$ must be integers when $\mathbf{R}$ is expressed in the coordinate system defined by $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. For a given point group restrictions on the primitive lattice vectors result in the seven crystal systems. Standard choices for the set $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ have been made for each crystal system and these will be adhered to in choosing a crystal coordinate system. In the cubic system the directions of $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are along the three equivalent and orthogonal rotation axes. In the triclinic system the choice of the directions of the lattice vectors is not determined by the point group symmetry of the crystal. This corresponds to the fact that in the triclinic system all even L lattice harmonics belong to the identity and may be chosen equal to the spherical harmonics.

Space groups may be classified into *symmorphic* space groups which have $\mathbf{t}=0$ and *nonsymmorphic* space groups which have $\mathbf{t}\neq 0$. Let us first consider the nature of the lattice sums occurring in the second and fourth moments for symmorphic space groups. In this case the symmetry operations of $(\mathcal{G})$ are proper or improper rotations plus translations which are lattice vectors so that $(S)\equiv(G)$, the point group of the crystal. The lattice sums occurring in Eq. (9) for the second moment are of the form

$$\frac{1}{N}\sum_{j\neq k}\frac{X_L^{1\alpha}(\bar{j}\bar{k})}{r_{jk}^6},$$

where the sum extends over all pairs of nuclei in the crystal. Let us define pairs of *physically* inequivalent nuclei as those whose lattice sites which may be brought into coincidence by a symmetry operation of $(\mathcal{G})$. *Chemically* inequivalent pairs of nuclei are those whose lattice sites cannot be brought into coincidence by such an operation. If now we consider the operation of elements of $(\mathcal{G})$ on the above sum we see that it may be reduced to the following form:

$$\frac{1}{\mathfrak{N}}\sum_{t\neq k}\frac{X_L^{1\alpha}(\bar{t}\bar{k})}{r_{tk}^6},$$

where $\mathfrak{N}$ is the total number of chemically inequivalent "like" nuclei in a unit cell, the index t runs over all chemically inequivalent nuclei in a unit cell, and the index k as before runs over all the nuclei in the crystal. It is clear that since the original sum is simply an average of the interactions between nuclear pairs taken over the entire crystal, due to the symmetry elements of (T) and (G), this is equal to the average over chemically inequivalent nuclei in a unit cell. A similar result is obtained for the lattice sums of Eqs. (17) and (18). The triple sum of Eq. (24a) may be written as

$$\frac{1}{\mathfrak{N}}\sum_{t\Delta}\frac{n_{t\Delta}}{d_\mu}\sum_{p}\frac{X_l^{\mu\alpha p*}(\bar{t}\bar{k})X_{l'}^{\mu\alpha' p}(\bar{t}\bar{n})}{r_{tk}^6 r_{tn} r_{kn}^5},$$

where the sum is over all triangles ($tkn\neq$) that can be formed at each distinct chemically inequivalent site t in a unit cell. The same results are valid for nonsymmorphic space groups, since the sums depend only on the distance vector $\mathbf{r}_{jk}$ between pairs of nuclei. Hence

$$[\mathbf{R},\mathbf{t}]\cdot\mathbf{r}_{jk}=[\mathbf{R},\mathbf{t}](\mathbf{r}_j-\mathbf{r}_k)=\mathbf{R}\cdot\mathbf{r}_{jk},$$

where $\mathbf{r}_j$ and $\mathbf{r}_k$ are expressed relative to some selected origin.

Let us now briefly consider the effect of the space group symmetry on the magnitude of the coefficients of identity representation lattice harmonics for a moment M_n and a fixed Laue group, i.e., a fixed number of irreducible components $N_n(G)$. The moment M_n is of the form

$$M_n=\textstyle\sum_{L\alpha} m_n{}^{L\alpha}X_L{}^{1\alpha}(\theta,\phi), \qquad (25)$$

where $m_n{}^{L\alpha}$ are the coefficients L takes on the $n+1$ values 0, 2, 4, $\cdots$ $2n$ and $L\alpha$ takes on $N_n(G)$ values. The quantities $m_n{}^{L\alpha}$ will vary with the number of distinct chemically inequivalent nuclei per unit cell and the space group ($\mathcal{G}$) as well as the lengths of lattice vectors. In principle it is possible to distinguish between different space groups with the same point group G on the basis of the magnitudes of the coefficients $m_n{}^{L\alpha}$ since the lattice sums will vary in magnitude with space group for a fixed $\mathfrak{N}$ and lattice vector lengths. An example of this will be given in the following section for the cubic system.

VI. APPLICATIONS OF MOMENT FORMULA

Although Van Vleck's formula has been applied extensively to a large number of solids, most experimental moment data have been obtained on polycrystalline solids. In this case, since all identity representation lattice harmonics except unity average to zero over a sphere the nth moment M_n is given by

$$(M_n)_{\text{powder}}=(1/4\pi)^{1/2}m_n{}^0,$$

where $m_n{}^0$ is the coefficient of $X_0{}^1$ in Eq. (25). As is immediately evident from Eq. (9) and using the results of the last section

$$(M_2)_{\text{powder}}=\frac{3}{5}\frac{\gamma^4\hbar^2I(I+1)}{\mathfrak{N}}\sum_{t\neq k}\frac{1}{r_{tk}{}^6},$$

(M_4) powder may be readily written down for cubic O_h symmetry from Eqs. (13), (16), (17), and (24a)–(24d), the coupling coefficients of Tables I and III, and the lattice harmonics of O_h as given by Bell[6] or von der Lage and Bethe.[5] One obtains

$(M_4)_{\text{powder}}$ (in rad^4 sec^{-4})

$$\begin{aligned}
&=\frac{9\gamma^8\hbar^4I^2(I+1)^2}{25d^{12}}\Bigg\{\bigg[\frac{7}{3}S^2(6,0)+\frac{4}{21}S^2(6,4)\bigg]\\
&-\bigg[\frac{3}{7}\bigg(\frac{14}{3}+\frac{3}{2}(I^2+I)^{-1}\bigg)S(12,0)\bigg]\\
&+\frac{6}{25}\bigg[\bigg({}_1S(615,00)+\frac{4}{49}\,{}_1S(615,44)\bigg)\\
&+\frac{4}{49}({}_3S(615,22)+{}_3S(615,44))\\
&+\frac{3}{7}\,{}_3S(435,22)+\frac{2}{7}\,{}_3S_\Delta(525,22)+\bigg(\frac{4}{49}\,{}_4S(615;22)\\
&+\frac{4}{49}\,{}_4S(615,44)+\frac{3}{7}\,{}_4S(435,22)+\frac{2}{7}\,{}_4S_\Delta(525;22)\bigg)\\
&+\frac{4}{49}\,{}_5S(615;44)-\frac{18}{49}\,{}_7S(525,33)-\frac{18}{49}\,{}_9S(525,33)\\
&-\bigg(\frac{22}{21}\,{}_{10}S(525,11)+\frac{18}{49}\,{}_{10}S(525;33)\bigg)\bigg]\Bigg\}, \qquad (26)
\end{aligned}$$

where the following notation has been used for the various sums

$${}_\alpha S(\beta,l)=\frac{(4\pi)^{1/2}}{\mathfrak{N}}\sum_{t\neq k}\frac{X_l{}^{1\alpha}(tk)}{r_{tk}{}^\beta},$$

and for sums involving products of lattice harmonics under the summation sign

$${}_{\mu\alpha\alpha'}S(\beta\gamma\delta,ll')=\frac{4\pi}{\mathfrak{N}}\sum_{t\Delta}\frac{n_{t\Delta}}{d_\mu}\sum_p\frac{X_l{}^{\mu\alpha p*}(\bar{t}\bar{k})X_{l'}{}^{\mu\alpha' p*}(\bar{t}\bar{n})}{r_{tk}{}^\beta r_{tn}{}^\gamma r_{kn}{}^\delta},$$

where the index μ labels the irreducible representation of the group O_h and runs from 1 to 10. A subscript Δ on S indicates that each term in the sum is multiplied by $\cos\theta_\Delta$. The ordering of the representations is the same as that given by Bell[6]; that is, $1\leftrightarrow s$, $2\leftrightarrow i$, $3\leftrightarrow d$, etc., where s, i, d, $\cdots$ are the symbols Bell[6] uses in labeling the representations. The terms inside the [ ] brackets are terms of type II, I, and III in the order in which they appear in Eq. (26). As will be shown presently, in the case of CaF$_2$ this is also the order of relatives magnitudes—terms of type II being the largest. For a lattice with only a small fraction f of the sites randomly occupied by magnetic nuclei terms of type I dominate since they depend linearly on f while terms of types I and II vary as f^2.

The angular dependence of the second and fourth moments has been experimentally studied in only a few instances. In the following, three examples of such studies are considered: calcium fluoride, for which second moment and a limited amount of fourth moment data are available, aluminum metal, and crystalline urea, for which a complete set of second moment data have been obtained.

A. Calcium Fluoride

Calcium fluoride single crystals have cubic O_h symmetry. Fluorine nuclei occupy the positions of a simple cubic lattice and the F^{19} isotope has spin $\frac{1}{2}$ and is 100% abundant.[12] The only stable magnetic nucleus of calcium appears to be the Ca^{43} which, however, is only 0.15% abundant.[12] The remaining calcium consists of the Ca^{40} (97.0%), Ca^{42} (0.6%), Ca^{44} (2.1%) and Ca^{48} (0.2%) isotopes.[12] The space group[13] of F nuclei only is O_h^1 while that of CaF_2 is O_h^5. The second moment may be written down at once from Eq. (9), Table II and the $L=0$, 4 identity representation lattice harmonics, in cubic O_h symmetry.

$$X_0^1=1/(4\pi)^{1/2},$$
$$X_4^1=(525/16\times 4\pi)^{1/2}(\tilde{x}^4+\tilde{y}^4+\tilde{z}^4-\tfrac{3}{5})$$

where $\tilde{x}$, $\tilde{y}$, and $\tilde{z}$ are the three direction cosines. Hence

$$M_2=(9/4)\gamma^4\hbar^2[(1/5)S(6,0)+(18/35)(1/9)S(6,4)\\ \times\{(525/16)^{1/2}(\tilde{x}^4+\tilde{y}^4+\tilde{z}^4-3/5)\}],$$

which may be rearranged to give

$$M_2=(9/8)(3/7)^{1/2}\gamma^4\hbar^2\{S(6,4)(\tilde{x}^4+\tilde{y}^4+\tilde{z}^4)\\ -[(3/5)S(6,4)-(2/5)(7/3)^{1/2}S(6,0)]\}.$$

The lattice sums may be evaluated by direct summation out to a given number of nearest neighbors and then approximation of the remaining terms by an integral. If the lower limit of the integral is chosen as the distance to the last lattice site included in the sum an upper limit to the sum is obtained. If the distance to nearest site not included in the sum is used a lower limit on the sum results. Carrying the direct summations out to 178 neighbors, one obtains by this method

$$S(6,0)=(8.399\pm 0.006)d^{-6},$$
$$S(6,4)=(12.65\pm 0.10)d^{-6},$$

where d is the lattice spacing parameter. Using these values of the sums M_2 is as follows:

$$M_2=9.315(\gamma^4\hbar^2/d^6)\{\tilde{x}^4+\tilde{y}^4+\tilde{z}^4-0.1952\}. \quad (27)$$

$\gamma(F^{19})=2.5167\times 10^4$ rad sec^{-1} G^{-1} (this is the gyromagnetic ratio for the F^{19} nucleus, not corrected for the Lamb diamagnetic shielding effect, which for F^{19} amounts to a correction of about 0.1%.) and from x-ray diffraction data[13] on CaF_2, the unit cell dimension is 5.451±0.001 Å and hence $d=2.7255\pm 0.0005$ Å. Hence

$$M_2=16.00\{\tilde{x}^4+\tilde{y}^4+\tilde{z}^4-0.1952\}, \quad (28)$$

where M_2 is in units of G^2.

The fourth moment for CaF_2 may also be computed. The angular variation will be expressed as lattice harmonics of the identity representation with $L=0$, 4, 6, and 8. The $L=0$ and 4 harmonics are given above. The necessary $L=6$ and 8 lattice harmonics are as follows:

$$X_6^1=(3\times 7\times 11/8)(2\times 13/4\pi)^{1/2}\\ \{\tilde{x}^2\tilde{y}^2\tilde{z}^2+(1/22)[X_4^1]-1/105\},$$
$$X_8^1=(5\times 13/16)(3\times 11\times 17/4\pi)^{1/2}\\ \times\{\tilde{x}^8+\tilde{y}^8+\tilde{z}^8-(28/5)[X_6^1]\\ -(210/143)[X_4^1]-1/3\}.$$

(The lattice harmonic X_8^1 is incorrect as given in reference 5. The last term in the second set of parentheses is shown there as $-\frac{1}{6}$ rather than the correct value $-\frac{1}{3}$.) $[X_L^1]$ indicates the unnormalized lattice harmonic, i.e., the terms in the second set of parentheses in the above expressions for X_L^1.

Type II terms may be computed from Eq. (19) and Table III without the evaluation of any additional lattice sums. The next largest contribution arises from terms of type I. The following lattice sums were evaluated for the nearest 26 neighbors and are within ±0.1% of the exact value.

$$S(12,0)=6.198,$$
$$S(12,4)=13.62,$$
$$S(12,6)=7.283,$$
$$S(12,8)=18.09,$$

in units of d^{-12}. This contribution to M_4 is evaluated directly from Eq. (17).

Terms of type III contribute the least to M_4 and require the most extensive computations as illustrated by Eq. (26). Necessary lattice sums over triangles have been evaluated for the nearest 26 neighbors by tabulating the quantities n_Δ, $r_{jk}{}^\alpha r_{jn}{}^\beta r_{kn}{}^\gamma$, and $\cos\theta_\Delta$ for the seventeen distinct triangle types that may be constructed (or a total number of triangles equal to $25\times 26=650$) and a table of values of the products of lattice harmonics which occur in the sums for each distinct type of triangle. The results of these calcu-

TABLE IV. Coefficients of lattice harmonics of M_4 contributed by terms of Types II, I, and III for CaF_2 in the rigid lattice approximation (G^4).

	X_0^1	X_4^1	X_6^1	X_8^1
Type II	413.3	337.6	46.0	44.0
Type I	−37.5	−39.2	−7.4	−7.6
Type III	3.6	−1.5	−0.7	−5.3
Total	379.4	296.9	37.9	31.1

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[12] D. Strominger, J. M. Hollander, and G. T. Seaborg, Revs. Modern Phys. **30**, 585 (1958).

[13] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. 1.

TABLE V. Root mean second and fourth moments for CaF_2—calculation and experiment (G).

Direction of H	$M_2^{1/2}$, calc Rigid lattice	$M_2^{1/2}$, calc Corrected for vibration	$M_2^{1/2}$, expt.[a]	$M_4^{1/4}$, calc	$M_4^{1/4}$, expt.[a]
[100]	3.59	3.68	3.49±0.20	4.29	4.16±0.16
[110]	2.21	2.30	2.21±0.10	2.68	2.70±0.08
[111]	1.49	1.59	1.55±0.06	1.82	1.92±0.07

[a] Reference 14.

lations are given in Table IV wherein the contribution of each type of term to the coefficient $m_4^{L\alpha}$ of X_L^1 is given. As is evident from the table the contribution of type I terms is about 1/7 that of type II terms, and the contribution of type III terms is generally less than 1–2% of the total due to terms of type I and II except for the contribution of type III terms to m_4^8 which is, in this case, about 1/7 of the contributions of terms of type I and II. A comparison of the available experimental second and fourth moment data[14] for the [100], [110], and [111] orientations of the crystal relative to the applied field and results the rigid lattice expressions of Eq. (27) and Table IV for these orientations is given in Table V. The values calculated in the rigid lattice approximation are generally in agreement with the experimental values within the experimental error. To check this agreement the second and fourth moments of polycrystalline, reagent grade calcium fluoride were determined in this laboratory. The results are given in Table VI along with the values computed for the rigid lattice. The experimental powder values of $M_2^{1/2}$ and $M_4^{1/4}$ are not equal to the rigid lattice values within the experimental error. To understand why this is the case let us consider the effect of lattice vibrations on the various lattice sums which enter into the moments. The quantities $1/r^6$, X_4^1/r^6, etc., occurring in the sums may be expanded in a Taylor series in the relative displacements of a pair of nuclei from their equilibrium positions. For $1/r^6$, one finds

$$\frac{1}{r^6}=\left(\frac{1}{r^6}\right)_0-6\sum_i\left(\frac{\bar{x}_i}{r^7}\right)_0\Delta x_i+\frac{1}{2}\sum_{ij}6\left(\frac{8\bar{x}_i\bar{x}_j-\delta_{ij}}{r^8}\right)_0\Delta x_i\Delta x_j+\cdots,\tag{29}$$

where the subscript 0 on a parenthesis indicates that the quantity inside the parenthesis is to be evaluated at the relative equilibrium positions of the nuclei. Clearly the time-average value of Δx_i is zero. In addition, we shall presently assume that $\langle\Delta x_i\Delta x_j\rangle_{\text{av}}=\delta_{ij}\langle\Delta^2\rangle_{\text{av}}$, where $\langle\Delta^2\rangle_{\text{av}}$ is a mean square amplitude of relative vibration of the nuclei. The assumption that the average value of cross products of the displacements such as $\langle\Delta x\Delta y\rangle_{\text{av}}$ are zero is exact for CaF_2 since such cross products vanish in O_h symmetry. The average value of $1/r^6$ then becomes

$$\left(\left\langle\frac{1}{r^6}\right\rangle_{\text{av}}\right)=\left(\frac{1}{r^6}\right)_0+3\sum_i\left(\frac{8\bar{x}_i^2-1}{r^8}\right)_0\langle\Delta^2\rangle_{\text{av}}$$
$$=(r^{-6})_0+15(r^{-8})_0\langle\Delta^2\rangle_{\text{av}}.\tag{30}$$

Evaluation of Eq. (30) for the first 26 nearest F^{19} neighbors in CaF_2 yields

$$\langle S(6,0)\rangle_{\text{av}}=S(6,0)_0+(90+11.2+1.5)\langle\Delta^2\rangle_{\text{av}}/d^2$$
$$=S(6,0)_0+102.7\langle\Delta^2\rangle_{\text{av}}/d^2.$$

In a similar manner $\langle S(6,4)\rangle_{\text{av}}$ and $\langle S(12,0)\rangle_{\text{av}}$ are evaluated to be as follows:

$$\langle S(6,4)\rangle_{\text{av}}=S(6,4)_0+(73.7-61.6)(5.728)\langle\Delta^2/d^2\rangle_{\text{av}}$$
$$=S(6,4)_0+69.3\langle\Delta^2/d^2\rangle_{\text{av}},$$
$$\langle S(12,0)\rangle_{\text{av}}=S(12,0)_0+408.9\langle\Delta^2/d^2\rangle_{\text{av}}.$$

Root mean square amplitudes of vibration of individual atoms may be calculated from the temperature dependence of intensities of x-ray diffraction maxima or from the Debye characteristic temperature of the solid. In NaF the root mean square amplitude $\langle\delta^2\rangle_{\text{av}}^{1/2}$ of the fluoride ion is equal to 0.195 Å. In CaF_2 the average root mean square amplitude is 0.12 Å.[15] Unfortunately, in the case of CaF_2 the root mean square amplitudes of the Ca^{++} and F^- ions are not separately known. If the average value of cross products of the individual atomic displacements is neglected, then

$$\langle\Delta^2\rangle_{\text{av}}=2\langle\delta^2\rangle_{\text{av}}.$$

i.e., the mean square amplitude of vibration of the relative nuclear coordinates is equal to twice the individual nuclear coordinates. Justification for this assumption is given in Appendix B. We have calculated the second and fourth moments of polycrystalline CaF_2

TABLE VI. Root mean second and fourth moments for polycrystalline CaF_2 (G).

	Expt.	Theory rigid lattice	Theory corrected for vibrations
$M_2^{1/2}$	2.65±0.03	2.55	2.63
$M_4^{1/4}$	3.37±0.08	3.22	3.30

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[14] C. R. Bruce, Phys. Rev. **107**, 43 (1957).

[15] K. Lonsdale, Acta. Cryst. **1**, 142 (1948).

using $\langle\Delta^2\rangle_{\text{av}}=0.040$ Å^2 corresponding to $\langle\delta^2\rangle_{\text{av}}^{1/2}=0.14$ Å. These values are given in the last column of Table VI. The agreement with experiment is now good and the values of M_2 calculated for the various orientations of a crystal are equal within experimental error to the values of Bruce.[14]

B. Aluminum Metal

Nuclear magnetic resonance of Al^{27} in aluminum metal has been studied extensively and recently second moment data have been obtained on single crystals.[16] Al metal is face-centered cubic and the necessary rigid lattice sums for the second moment are as follows:

$$S(6,0)=(115.5\pm0.4)d^{-6},$$
$$S(6,4)=(-44.9\pm1.4)d^{-6},$$

where d is now the length of the edge of the cubic unit cell (there are 4 Al atoms per unit cell). The direct summations were carred out for the 176 nearest neighbors. M_2 may be immediately written down from Eq. (12).

$$M_2=-385.5(\gamma^2\hbar^2/d^6)(\tilde{x}^4+\tilde{y}^4+\tilde{z}^4-2.173).$$

$\gamma=6.970\times10^3$ G^{-1} rad sec^{-1} and $d=4.0415$ Å at 298°K.[13] Hence, the rigid-lattice second moment is (in G^2)

$$M_2=-4.780\{\tilde{x}^4+\tilde{y}^4+\tilde{z}^4-2.173\}.$$

Values of M_2 calculated from this expression are given in Table VII and may be seen to be considerably less than the experimental values for all orientations.

The mean square amplitude of vibration in Al metal has been calculated[15] from the Debye temperature to be equal to 0.033 Å^2 at 293°K. Once again we may correct the values of $S(6,0)$ and $S(6,4)$ for this effect as before, using $\langle\Delta^2\rangle_{\text{av}}=0.066$ Å^2:

$$\langle S(6,0)\rangle_{\text{av}}=S(6,0)_0+3041\langle\Delta^2\rangle_{\text{av}}/d^8=127.8d^{-6},$$
$$\langle S(6,4)\rangle_{\text{av}}=S(6,4)_0-494\langle\Delta^2\rangle_{\text{av}}/d^8=-46.9d^{-6},$$

where 42 nearest neighbors have been considered. Using these values of the lattice sums the second moment is as follows:

$$M_2=-4.996[\tilde{x}^4+\tilde{y}^4+\tilde{z}^4-2.265]\ \text{G}^2.$$

TABLE VII. Experimental, rigid lattice, and vibration-corrected values of the second moment of aluminum metal at 298°K.

Direction of H	M_2, G^2 Expt.	M_2, G^2 Theory, rigid lattice	M_2, G^2 Theory, corrected for vibrations
[100]	6.7±0.6[a]	5.61	6.32
[110]	9.9±1.2[a]	8.00	8.82
[111]	10.0±1.0[a]	8.80	9.65
Powder	9.8±1.2[b]	7.52	8.32

[a] See reference 16.
[b] J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959).

Values of M_2 calculated from this expression are also given in Table VII and are in much better agreement with the experimental values than are those for the rigid lattice.

C. Urea

The space group of area, CO(NH$_2$)$_2$, is $D_{2d}{}^3$ (tetragonal, point group D_{2d}) and there are two molecules in the unit cell. X-ray diffraction data[17] have yielded the positions of C, O, and N in the unit cell, but little direct information on the positions of the protons. The two carbon and two oxygen atoms are in special positions (c): $(0,\frac{1}{2},z)$ and $(\frac{1}{2},0,\bar{z})$. The four nitrogen atoms are in special positions (e): $(x,\frac{1}{2}+x,z)$, $(\bar{x},\frac{1}{2}-x,z)$, $(\frac{1}{2}+x,\bar{x},\bar{z})$ and $(\frac{1}{2}-x,x,\bar{z})$. The eight protons per unit cell must also be in two sets of positions (e) and hence *four* parameters x_1, z_1 and x_2, z_2 are necessary to locate the two chemically inequivalent sets of protons per unit cell.

Second moments of the proton magnetic resonance absorption at 300°K have been reported by Andrew and Hyndman[18] for various directions of **H** in the planes perpendicular to the tetragonal axis [001] and the axis [110].

By reference to Table I it is seen that *four* independent parameters are necessary to completely specify M_2 in D_{2d} symmetry. The necessary lattice harmonics may be easily ascertained from reference 6 to be as follows:

$$\begin{aligned}X_0{}^1&=(4\pi)^{-1/2}[1],\\X_4{}^{1,1}&=(525/16\times4\pi)^{1/2}[\tilde{x}^4+\tilde{y}^4+\tilde{z}^4-\tfrac{3}{5}],\\X_2{}^1&=(5/4\times4\pi)^{1/2}[2\tilde{z}^2-\tilde{x}^2-\tilde{y}^2],\\X_4{}^{1,2}&=(735/16\times4\pi)^{1/2}[2\tilde{z}^4-\tilde{x}^4-\tilde{y}^4-6/7[X_2{}^1]],\end{aligned}\tag{31}$$

where $[X_2{}^1]=2\tilde{z}^2-\tilde{x}^2-\tilde{y}^2$.

The angular dependence of M_2 in the planes perpendicular to [001] and [110] may be obtained by projection of the lattice harmonics:

$$\begin{aligned}M_2{}^{001}=[m_1+(3/20)m_4{}^{(1)}-m_2+(3/28)m_4{}^{(2)}]\\+(\tfrac{1}{4}m_4{}^{(1)}-\tfrac{1}{4}m_4{}^{(2)})\cos4\phi_0,\end{aligned}\tag{32}$$

$$\begin{aligned}M_2{}^{110}=[m_1-(3/80)m_4{}^{(1)}+\tfrac{1}{2}m_2+(15/112)m_4{}^{(2)}]\\+[\tfrac{1}{4}m_4{}^{(1)}+\tfrac{3}{2}m_2-(1/28)m_4{}^{(2)}]\cos2\psi_0\\+[\tfrac{3}{16}m_4{}^{(1)}+\tfrac{3}{16}m_4{}^{(2)}]\cos4\psi_0,\end{aligned}\tag{33}$$

where the triplet of superscripts on M_2 indicates the rotation axis, ϕ_0 is the rotation angle around [001] measured relative to the [100] direction and ψ_0 is the rotation angle around [110] measured relative to the [001] direction. The coefficients $m_L{}^\alpha$ are, for convenience, presently defined as the coefficients of the unnormalized lattice harmonics $[X_L{}^{1\alpha}]$ [defined as the expressions in the square brackets of (31)] occurring

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[16] P. L. Sagalyn and J. A. Hofmann, Phys. Rev. **127**, 68 (1962).

[17] P. Vaughan and J. Donohue, Acta. Cryst. **5**, 530 (1952).

[18] E. R. Andrew and D. Hyndman, Discussions Faraday Soc. **19**, 195 (1955).

in the expression for M_2, i.e.,

$$M_2=\sum_{L\alpha} m_L^{(\alpha)}[X_L^{1\alpha}(\theta,\phi)].$$

From the data given by Andrew and Hyndman the following values are obtained for the quantities $m_L^{(\alpha)}$

$$m_0=20.1\pm0.4\ \mathrm{G}^2,$$
$$m_4^{(1)}=-3.3\pm1.1\ \mathrm{G}^2,$$
$$m_2=4.3\pm0.1\ \mathrm{G}^2,$$
$$m_4^{(2)}=5.9\pm1.1\ \mathrm{G}^2.$$

Each $m_L^{(\alpha)}$ is, of course, directly proportional to a lattice sum $S(6,L\alpha)$, which in turn is a function of the parameters x_1, z_1, x_2, and z_2 needed to specify the positions of the protons. Since there are four *independent* $m_L^{(\alpha)}$ one may determine the values of the four parameters which yield values of the quantities $m_L^{(\alpha)}$ that are equal to the experimental values given above.

This was done by first calculating the quantities $m_L^{(\alpha)}$ for a selected set of proton coordinates. These were chosen such that the bond lengths N_1-H_1, N_1-H_2 were equal to those given by Andrew and Hyndman[18] and the bond angles $H_1N_1H_2$ and CN_1H_1 were equal to 120° where the numbering system employed is shown in Fig. 3. These authors assumed that the lengths of bonds N_1-H_1 and N_1-H_2 were equal. All lattice sums were carried out directly for all protons neighbors within a 4.8 Å radius for each of the two chemically inequivalent protons. For the inner protons (1) the number of such neighbors is 22 while for the outer protons (2) the number of such neighbors is equal to 27. The remaining contribution to the sums was estimated by the continuum approximation. The error involved in sums computed in this way is less than 0.5%. Next, the first partial derivatives of each $m_L^{(\alpha)}$ with respect to each of the proton coordinates were calculated. This was done by displacing the coordinate x_1 by 0.02 Å and computing new values of the $m_L^{(\alpha)}$. It was found that only the intramolecular contributions to the sums contributed significantly to the differential coefficients and the remaining coefficients were evaluated by calculating the change in the intramolecular contribution to a given sum. A set of four simultaneous equations were then solved to obtain values of the proton coordinates which yield values of the $m_L^{(\alpha)}$ in agreement with the experimental values. Values of the initial and final proton coordinates, bond lengths, and the $H_1N_1H_2$ bond angle are listed in Table VIII. The errors accompanying the final values are the accumulated probable errors derived from the estimated probable error of the data given by Andrew and Hyndman.[18] With experimental uncertainty the outer $N-H$ bond distance is determined to be longer than the inner $N-H$ bond distance.

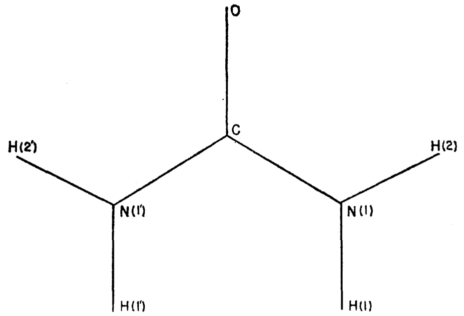

FIG. 3. Urea molecule.

The effect of nuclear motions on the results of Table VIII is uncertain due to the lack of direct information on nuclear motions in the solid. Measurements[19] of the linewidth of urea above 25° exhibit a motional narrowing phenomena in the neighborhood of 50°C which is ascribed to rotation of the NH_2 groups about the $C-N$ bonds. These authors obtain a value of $m_0=20.8\pm0.6\ \mathrm{G}^2$ at 0°C which overlaps with the value obtained above from the data of Andrew and Hyndman.[18] However, little is presently known concerning the temperature variation of the other quantities particularly $m_4^{(1)}$ and $m_4^{(2)}$. In view of the motional narrowing process which sets in at temperatures just above 25°C it is likely that the mean square amplitudes of proton displacements out of the xy plane are not insignificant and the various sums should be corrected for this effect. However, in view of the present lack of detailed knowledge concerning the mean square amplitudes of such motions we have refrained from attempting the correction. Infrared spectra[20] obtained with polarized radiation indicate that the inner and outer hydrogens are not equivalent. The symmetric $N-H$ stretching bands appear to differ in energy by only 20 cm^{-1}. This small energy difference may indicate a correspondingly small difference in the bond lengths N_1-H_1 and N_1-H_2.

TABLE VIII. Initial and final proton coordinates (Å), NH Bond lengths (Å), and $H_1N_1H_2$ bond angle for urea.

	x_1	z_1	x_2	z_2	N_1-H_1	N_1-H_2	H_1-H_2	$\angle H_1N_1H_2$
Initial	0.809	−0.175	1.450	1.394	1.046	1.046	1.812	120°
Final	0.824±0.014	−0.153±0.013	1.493±0.015	1.363±0.023	1.024±0.017	1.085±0.026	1.787±0.026	116°±4°

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[19] R. A. Kromhout and W. G. Moulton, J. Chem. Phys. **23**, 1673 (1955).
[20] R. D. Waldron and R. M. Badger, J. Chem. Phys. **18**, 566 (1950).

VII. FURTHER APPLICATIONS

A. Effect of Applied Electric Fields

As was pointed out in Secs. II and III and may be seen from Table I, the moments produced by dipolar interactions do not allow proper crystal point groups to be distinguished from the corresponding (isomorphic) improper point groups. In principle, this ambiguity may be partially resolved by measurement of the moments in the presence of a strong electrostatic field applied to the crystal. If the crystal does not have a center of inversion symmetry, the moments may be altered by the presence of the applied electric field but cannot be altered in the presence of a center of inversion. This may be seen by consideration of the change $\delta m_n{}^{L\alpha}$ of the quantities $m_n{}^{L\alpha}$ of Eq. (25) produced by the applied electric field:

$$\delta m_n{}^{L\alpha}=\sum_i R_{ni}{}^{L\alpha}E_i, \tag{34}$$

where the E_i are the components of the applied electric field along the crystal coordinate system and $R_{ni}{}^{L\alpha}$ is a tensor quantity. Applying the inversion operator $\mathcal{I}$ to both sides of Eq. (34), one obtains

$$\begin{aligned}\mathcal{I}\delta m_n{}^{L\alpha}=\delta m_n{}^{L\alpha}&=\sum(\mathcal{I}R_{ni}{}^{L\alpha}\mathcal{I}^{-1})\mathcal{I}E_i\\&=-\sum(\mathcal{I}R_{ni}{}^{L\alpha}\mathcal{I}^{-1})E_i.\end{aligned} \tag{35}$$

The quantity $R_{ni}{}^{L\alpha}$ depends only the crystal symmetry and if the crystal has a center of inversion, $(\mathcal{I}R_{ni}{}^{L\alpha}\mathcal{I}^{-1})=R_{ni}{}^{L\alpha}$ and $\delta m_n{}^{L\alpha}\equiv 0$. If no center of inversion is present, $\delta m_n{}^{L\alpha}$ need not be zero.[20a]

B. Spectroscopy of Solids

As mentioned in the introduction, lattice harmonics are ideally suited to represent the angular dependence of physical quantities in the case that the source object possesses nontrivial symmetry.

Although the group-theory method has been used extensively to derive selection rules in spectroscopy, little use appears to have been made of the basis functions of the group involved, i.e., the lattice harmonics, to derive the angular dependence of intensities. In optical and magnetic resonance spectroscopy the intensity of absorbed or emitted radiation may be measured at a definite frequency as a function of crystal orientation. In the case of optical (electric dipole or electric quadrupole) spectroscopy, lattice harmonics can be used to specify the intensity as a function of the orientation of the electric vector of the absorbed or emitted light relative to the crystal axes. Similarly, the number of independent parameters needed to specify the angular dependence of the intensity can be readily derived. In quadrupole spectroscopy and electron paramagnetic resonance spectroscopy, the moment method can also be used to characterize spectra and the angular dependence of the moments expressed as lattice harmonics which are functions of the orientation of the applied field relative to the crystal axes. Details of these and other applications of the lattice harmonics method in spectroscopies of the solid state are under consideration.

APPENDIX A

The lattice harmonics coupling coefficients may be defined as follows:

$$\begin{aligned}&X_l{}^{\mu\alpha i}(\theta,\phi)X_{l'}{}^{\mu'\alpha'i'*}(\theta,\phi)\\&\quad=\sum_{L,U,A,I}\langle l(\mu\alpha)i,l'(\mu'\alpha')i'|LUAI\rangle X_L{}^{UAI}(\theta,\phi).\end{aligned} \tag{A1}$$

These coefficients are analogous to the Clebsch-Gordan coefficients and may be written in terms of the latter using the matrix elements of $\mathbf{U}_L$ defined by Eq. (8).

For the study of moments, it is only necessary to study cases where the lattice harmonics on the right side of (A1) belong to the identity representation. In particular, it can be shown that $\sum_i X_l{}^{\mu\alpha i}(\theta,\phi)\times X_{l'}{}^{\mu\alpha' i*}(\theta,\phi)$ is invariant toward any rotation belonging to the point group, and therefore may be written as a sum of lattice harmonics belonging to the identity representation only:

$$\begin{aligned}&\sum_i X_l{}^{\mu\alpha i}(\theta,\phi)X_{l'}{}^{\mu\alpha' i*}(\theta,\phi)\\&\qquad=\sum_{L,A}\langle l(\mu\alpha),l'(\mu\alpha')|LA\rangle X_L{}^{1A}(\theta,\phi),\end{aligned} \tag{A2}$$

where $\langle l(\mu\alpha),l'(\mu\alpha')|LA\rangle=\sum_i\langle l(\mu\alpha)i,l'(\mu'\alpha')i|L1A\rangle$.

The proof is as follows. Applying a rotation operator R which belong to the point group to the left side of (A2), we get

$$\begin{aligned}&\sum_i P_R X_l{}^{\mu\alpha i}(\theta,\phi)P_R X_{l'}{}^{\mu\alpha' i*}(\theta,\phi)\\&\quad=\sum_{i,p,q}D^{(\mu)}(R)_{pi}X_l{}^{\mu\alpha p}(\theta,\phi)D^{(\mu)*}(R)_{qi}X_{l'}{}^{\mu\alpha' q*}(\theta,\phi)\\&\qquad=\sum_p X_l{}^{\mu\alpha p}(\theta,\phi)X_{l'}{}^{\mu\alpha' p*}(\theta,\phi).\end{aligned}$$

The last step follows from the unitarity of our representation, $\sum_i D^{(\mu)}(R)_{pi}D^{(\mu)*}(R)_{qi}=\delta_{pq}$.

Using the orthogonality property between the lattice harmonics, the coupling coefficients can be obtained by multiplying both sides of (A2) by $X_L{}^{1A*}(\theta,\phi)$ and integrating over all space

$$\begin{aligned}&\langle l(\mu\alpha),l'(\mu\alpha')|LA\rangle\\&\quad=\int_{\text{all space}}\sum_i X_l{}^{\mu\alpha i}(\theta,\phi)X_{l'}{}^{\mu\alpha' i*}(\theta,\phi)\\&\qquad\qquad\times X_L{}^{1A*}(\theta,\phi)d\Omega.\end{aligned} \tag{A3}$$

The lattice harmonics on the right side of (A3) may be expanded in terms of spherical harmonics by (8), and

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[20a] *Note added in proof.* For solids of low dielectric constant, the nuclear displacements resulting from an external electric field of 10 kV cm^{-1} are of the order of 10^{-4} to 10^{-6} Å. Any changes in the second or fourth moments are probably too small to be observed except for solids of high dielectric constant such as ferroelectrics.

we get

$$\langle l(\mu\alpha),l'(\mu\alpha')|LA\rangle$$

$$=\sum_{m,m',M} U_{\mu\alpha im}{}^{l}U_{\mu\alpha' im'}{}^{l'*}U_{1AM}{}^{L*} \times\int Y_{lm}Y_{l'm'}{}^{*}Y_{LM}{}^{*}d\Omega$$

$$=\sum_{m,m'} U_{\mu\alpha im}{}^{l}U_{\mu\alpha' im'}{}^{l'*}U_{1A,m-m'}{}^{L*}\beta_{l}^{-1}\beta_{l'}\beta_{L} \times C(l'Ll;00)C(l'Ll;m',m-m'). \quad \text{(A4)}$$

Note that (A4) is identical to (23).

The coupling coefficients $\langle l(\mu\alpha),l'(\mu\alpha')|LA\rangle$ may be evaluated either by direct integration as given in (A3) or by (A4) via the Clebsch-Gordan and transformation coefficients. Both methods are somewhat cumbersome. Often the coefficients may be easily evaluated by inspection of the equation

$$\sum_i X_{l}{}^{\mu\alpha i}(\tilde{x},\tilde{y},\tilde{z})X_{l'}{}^{\mu\alpha' i*}(\tilde{x},\tilde{y},\tilde{z}) =\sum_{LA}\langle l(\mu\alpha)l'(\mu\alpha')|LA\rangle X_{L}{}^{1A}(\tilde{x},\tilde{y},\tilde{z}),$$

with the use of identities such as

$$\tilde{x}^4+\tilde{y}^4+\tilde{z}^4\equiv 1-2(\tilde{x}^2\tilde{y}^2+\tilde{y}^2\tilde{z}^2+{}^2\tilde{z}\tilde{x}^2),$$

and

$$2(\tilde{x}^4\tilde{y}^4+\tilde{y}^4\tilde{z}^4+\tilde{z}^4\tilde{x}^4)\equiv 1+(\tilde{x}^8+\tilde{y}^8+\tilde{z}^8) -8\tilde{x}^2\tilde{y}^2\tilde{z}^2-2(\tilde{x}^4+\tilde{y}^4+\tilde{z}^4).$$

For example, for cubic O_h symmetry with $\mu=4$, $l=l'=2$ one has (normalized to 4π), $\alpha=\alpha'=1$

$$X_2{}^{411}=(15)^{1/2}\tilde{y}\tilde{z},\quad X_2{}^{412}=(15)^{1/2}\tilde{z}\tilde{x},\quad X_2{}^{413}=(15)^{1/2}\tilde{x}\tilde{y},$$

and, hence,

$$15(\tilde{x}^2\tilde{y}^2+\tilde{y}^2\tilde{z}^2+\tilde{z}^2\tilde{x}^2)=(15/2)[1-(\tilde{x}^4+\tilde{y}^4+\tilde{z}^4)] =-(15/2)[X_4]+3.$$

Thus

$$(4\pi)^{1/2}\langle 2(41)2(41)|41\rangle=-(12/7)^{1/2},$$

$$(4\pi)^{1/2}\langle 2(41)2(41)|11\rangle=3.$$

For cubic O_h symmetry, the lattice harmonics coupling coefficients that are needed to evaluate the fourth moment have been tabulated in Table III.

APPENDIX B

In the consideration of lattice vibrations in Secs. VIA and VIB, the following assumption was made:

$$\langle\Delta^2\rangle_{\text{av}}=2\langle\delta^2\rangle_{\text{av}}, \quad \text{(B1)}$$

where $\langle\Delta^2\rangle_{\text{av}}$ is the mean square amplitude of Δx_i for a nuclear pair and $\langle\delta^2\rangle_{\text{av}}$ is the corresponding quantity for an individual nucleus. In this Appendix, the validity of this assumption will be examined. Equation (B1) is strictly true if the nuclei are considered to vibrate independently of one another, such as for an Einstein model of the lattice vibrations. In the following, the nature of this approximation will be briefly considered for the Debye model.

The approximation of Eq. (B1) may be rewritten as follows:

$$\langle[x_i{}^{\alpha}(n)-x_i{}^{\alpha}(n')]^2\rangle=\langle x_i{}^{\alpha}(n)x_i{}^{\alpha}(n)\rangle +\langle x_i{}^{\alpha}(n')x_i{}^{\alpha}(n')\rangle. \quad \text{(B2)}$$

$x_i{}^{\alpha}(n)$ denotes the displacement along the ith cartesian coordinate ($i=1, 2, 3$) of the αth atom in the nth unit cell [$n=(n_1, n_2, n_3)$] from its equilibrium position and the angular bracket denotes the time and canonical ensemble average value. $x_i{}^{\alpha}(n)$ may be expanded in normal $\xi_{iq}{}^{\alpha}(\mathbf{k})$ as follows[21]:

$$x_i{}^{\alpha}(n)=\sum_{\mathbf{k}q} a_q(\mathbf{k})\xi_{iq}{}^{\alpha}(\mathbf{k}) \times\exp[i(\mathbf{k}\cdot\mathbf{r}^{\alpha}(n)-\omega_q(\mathbf{k})t)]. \quad \text{(B3)}$$

$a_q(k)$ is the amplitude of the qth mode with wave vector k, q is the mode index ($q=1, \cdots 3N$), and $\omega_q(\mathbf{k})$ is the angular frequency of the qth mode at wave vector $\mathbf{k}$. If the quantity on the left of Eq. (B2) is written out in full, one obtains

$$\langle[x_i{}^{\alpha}(n)-x_i{}^{\alpha}(n')]^2\rangle=\langle x_i{}^{\alpha}(n)x_i{}^{\alpha}(n)\rangle +\langle x_i{}^{\alpha}(n')x_i{}^{\alpha}(n')\rangle-2\langle x_i{}^{\alpha}(n)x_i{}^{\alpha}(n')\rangle.$$

From Eq. (B3) we obtain an expression for $x_i{}^{\alpha}(n)x_i{}^{\alpha}(n)$ as follows:

$$x_i{}^{\alpha}(n)x_i{}^{\alpha}(n)=\sum_{\mathbf{k},\mathbf{k}'q,q'} \xi_{iq}{}^{\alpha}(\mathbf{k})\xi_{iq'}{}^{\alpha}(\mathbf{k}')^{*}a_q(\mathbf{k})a_{q'}(\mathbf{k}')^{*} \times\exp\{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}^{\alpha}(n)-[\omega_q(\mathbf{k})-\omega_{q'}(\mathbf{k}')]t\}.$$

After taking the time and canonical ensemble average one obtains

$$\langle x_i{}^{\alpha}(n)x_i{}^{\alpha}(n)\rangle=\langle x_i{}^{\alpha}(n')x_i{}^{\alpha}(n')\rangle =\sum_{\mathbf{k}q}|a_q(\mathbf{k})|^2|\xi_{iq}{}^{\alpha}(\mathbf{k})|^2. \quad \text{(B4)}$$

Likewise, we obtain

$$\langle x_i{}^{\alpha}(n)x_i{}^{\alpha}(n')\rangle=\sum_{\mathbf{k}t}|a_q(\mathbf{k})|^2|\xi_{iq}{}^{\alpha}(\mathbf{k})|^2 \times\exp\{i\mathbf{k}\cdot[\mathbf{r}^{\alpha}(n)-\mathbf{r}^{\alpha}(n')]\}. \quad \text{(B5)}$$

In order to justify Eq. (B1) it is necessary to show that $\langle x_i{}^{\alpha}(n)x_i{}^{\alpha}(n')\rangle$ is small compared to $\langle x_i{}^{\alpha}(n)x_i{}^{\alpha}(n)\rangle$. Let us consider a cubic, monatomic substance with one atom per unit cell ($\alpha=1$). The mean square amplitude of the quantity $a_q(\mathbf{k})\xi_{iq}{}^{\alpha}(\mathbf{k})$ is the same as that of a harmonic oscillator in thermal equilibrium.[22]

$$\langle|a_q(\mathbf{k})\xi_{iq}(\mathbf{k})|^2\rangle=\frac{\hbar}{kmNv_q}\left[\frac{1}{2}+\frac{1}{e^{\hbar v_q k/\kappa T}-1}\right],$$

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[21] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 3.

[22] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell & Sons, London, 1948), Chap. 5.

where N is the total number of atoms in the crystal, v_q is the velocity of the qth mode, (i.e., transverse or longitudinal), κ is the Boltzmann constant and T is temperature. The sums over $\mathbf{k}$ in Eqs. (B4) and (B5) may be replaced by integrals as follows:

$$\sum_k F_q(k) \to \int_0^{k_{mq}} F_q(k) f_q(k) d\tau_k,$$

$f_q(k)$ is the density of wave vector $\mathbf{k}$ for the qth mode, $d\tau_k$ is a spherical volume element in k space, and k_{mq} is a maximum possible value of k for the qth mode. In the Debye model

$$f_q(k) = V/8\pi^3,$$

where V is the volume of the crystal. Thus for the sums of Eqs. (B4) and (B5) one obtains

$$\begin{aligned}\langle x_i(n)x_i(n)\rangle &= \sum_q 3\frac{\hbar}{v_q k_{mq}{}^3 m}\int_0^{k_{mq}}\left[\frac{1}{2}+\frac{1}{e^{\hbar v_q k/\kappa T}-1}\right]kdk\\ &= \sum_q \frac{3\hbar}{v_q k_{mq} m}\left[\frac{1}{4}+\frac{T^2}{\theta_q{}^2}\int_0^{\theta_q/T}\frac{\xi d\xi}{e^{\xi}-1}\right], \qquad \text{(B6)}\end{aligned}$$

where $\theta_q = \hbar k_{mq} v_q / K$ and m is the atomic mass.

$$\langle x_i(n)x_i(n')\rangle = \sum_q \frac{3\hbar}{2mv_q k_{mq}{}^3}\int_0^{k_{mq}}\int_0^{\pi}\left[\frac{1}{2}+\frac{1}{e^{\hbar v_q k/\kappa T}-1}\right] \times e^{ikr_n \cos\theta} k \sin\theta d\theta dk, \qquad \text{(B7)}$$

where $\mathbf{r}_n = |\mathbf{r}(n) - \mathbf{r}(n')|$.

The integration over θ may be performed in Eq. (B7) as well as the k integration of the first term of the integrand.

$$\begin{aligned}\langle x_i(n)x_i(n')\rangle = \sum_q \Bigg[&\frac{3}{2}\frac{\hbar}{mv_q k_{mq}}\frac{1-\cos k_{mq} r_n}{(k_{mq} r_n)^2}\\ &+\frac{3\hbar}{mv_q k_{mq}(k_{mq} r_n)}\frac{T}{\theta_q}\int_0^{\theta_q/T}\frac{\sin\beta_q\xi}{e^{\xi}-1}d\xi\Bigg], \qquad \text{(B8)}\end{aligned}$$

where $\beta_q = k_{mq} r_n T/\theta_q$.

There are two simple methods for the evaluation of k_{mq}. In the first, or Debye's method, the total number of waves up to a given frequency ω_m is set equal to $3N$. This yields

$$\omega_m = 2\pi v(3N/4\pi V)^{1/3},$$

and hence

$$k_{mq} = 2\pi(v/v_q)(3N/4\pi V)^{1/3},$$

where v is a mean velocity defined by

$$3/v^3 = 1/v_l{}^3 + 2/v_t{}^3.$$

The other method, that of Born, is obtained by setting the total number of waves up to a given wave number k_m equal to $3N$

$$k_m = 2\pi(3N/4\pi V)^{1/3},$$

k_m defined in this way is independent of q.

In aluminum metal (face-centered cubic structure) the transverse and longitudinal velocities of sound are nearly equal and for purposes of estimation we shall take $v_t = v_l = 6\times10^5$ cm sec^{-1}. The Debye temperature $\theta_D = 390$°K. Let the nearest-neighbor distance be a, then

$$V = Na^3\sqrt{2}, \quad\text{and}\quad k_m = 0.70(2\pi/a).$$

At very low temperatures only the first terms in Eqs. (B6) and (B8) are nonzero and one finds

$$\left[\frac{\langle x_i(n)x_i(n')\rangle}{\langle x_i(n)x_i(n)\rangle}\right]_{T=0°\mathrm{K}} = \frac{2(1-\cos k_m r_n)}{(k_m r_n)^2} = 0.14,$$

for $r_n = a$, the nearest-neighbor distance. At 300°K, the remaining terms may be evaluated by graphical integration. For nearest neighbors, the result is

$$\left[\frac{\langle x_i(n)x_i(n')\rangle}{\langle x_i(n)x_i(n)\rangle}\right]_{T=300°\mathrm{K}} = 0.36.$$

Thus, the approximation expressed by Eq. (B1) is reasonably accurate for Al at 0°K but becomes somewhat poorer at 300°K for first nearest neighbors. For more distant nuclear pairs, Eq. (B1) becomes more nearly exact.

The detailed lattice vibration frequency spectrum for aluminum has been experimentally measured by Walker.[23] Calculated values of $\langle x_i(n)x_i(n')\rangle / \langle x_i(n)x_i(n)\rangle$ for nearest neighbors at 0 and 300°K using the detailed spectrum are not much different from the Debye values given above.

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[23] C. B. Walker, Phys. Rev. **103**, 547 (1956).