Quadrupole Interaction in Crystals

Ojiro NAGAI and Tuto NAKAMURA*

Department of Physics, Kyusyu University, Fukuoka

The quadrupole array for the lowest energy of quadrupole interaction in crystals is obtained by generalizing Luttinger and Tisza's theory of dipole interaction. The theory is presented for the two kinds of problems: the simplest case of quadrupole pertaining to a doubly degenerate orbital e_g and the other general cases both for the cubic crystals. In the former case, the quadrupole interaction is written in terms of fictitious spins, whence we can get the solution of lowest energy classically, serving to obtain some informations of the orbital ordering in compounds with Mn^{3+}, Cu^{2+} and Cr^{2+}. In the latter cases, the five components of the quadrupole are totally effective, leading to a rather complicated problem. The classical solution is, however, easily obtained, though somewhat complicated. The quadrupole array of lowest energy in face-centered cubic lattice proves to be realized in molecular crystals N_2, N_2O, CO_2 and CO, which is accompanied with large quadrupole but without or with small dipole moment.

§ 1. Introduction

In this paper, we shall look for the quadrupole array in a cubic crystal which brings about the lowest energy of quadrupole interactions. There are some interesting applications of the results obtained.

Firstly, the crystal structures and the configuration of molecular orientation for many molecular crystals have been found by the X-ray analysis. It is known that molecular crystals composed of linear molecules N_2, N_2O, CO_2 and CO show the same type of ordering of molecular orientation at low temperatures, being crystallized in F.C.C. lattice.** Between two molecules, there are three or more kinds of anisotropic interactions in general, that is, the valence, van der Waals and multipole interactions. We shall consider here the non-polar molecule with considerable magnitude of quadrupole moment. Therefore the quadrupole-quadrupole interaction will be much effective. It is known that between two hydrogen molecules the directional dependence of both the van der Waals and valence forces are considerably smaller than that of the quadrupole interactions, which proves to be predominantly effective in causing the orientational ordering of ortho-hydrogen.[1] Due to this situation, we are inclined to think that the orientational ordering of molecules in the crystals mentioned will mainly come from the molecular quadru-

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* Present address: Department of Physics, Osaka University, Osaka.
** Hereafter S.C., B.C.C. and F.C.C. lattices mean simple cubic, body-centered cubic and face-centered cubic lattices respectively.

pole interaction. In fact, we shall see later that the molecules N_2, N_2O, CO_2 and CO have such magnitude of quadrupole moment that the orientational ordering of molecule in crystal is explained satisfactorily from its quadrupole interaction. Moreover, our predicted array proves to be just in the actual situation.

Secondly, there have appeared a theory of magnetic anisotropy related to the cobaltous and ferrous oxides, where Co^{2+} and Fe^{2+} in cubic field have a large orbital momentum unquenched, hence a large multipole interaction results.[2] The study of preferential array of quadrupole may give some informations about such problem. Now the magnetic property associated with the d-electron states in the metal ions of perovskite type compound $LaMnO_3$ and deformed perovskite type MnF_3 has been one of the recent interesting problems.[3] Their magnetic structure is said to be the " A "-type structure in which spins in a c-plane are coupled ferromagnetically and spins of two adjacent planes are coupled antiferromagnetically. The magnetic ordering of these compounds should be explained by assuming appropriate ordering of e_g-orbitals. It is well-known that a five-fold degenerate d-level in cubic crystalline field splits into a doubly degenerate e_g-level and a triply degenerate t_{2g}-level. Since the level splitting is of the order of magnitude of $10^4 \, cm^{-1}$, we have only to take up the interaction within the lowest manifold. In the case of Mn^{3+} ion, e_g-level is lower, because the electron configuration of Mn^{3+}, $(3d)^4$, is equivalent to the ion with a d-hole in the Hund lowest state, hence the level order is reversed. In the above compounds, the orbital ordering will be caused at first by the interaction between the displacement of anion and e_g-electron but the effect of quadrupole interaction of e_g-electron which will be treated in Sections 3 and 4 is not so small. Therefore it seems to be worthwhile to find the ordering of e_g-orbitals with the lowest energy.

In the present paper, we shall look for the quadrupole array with the lowest energy in cubic crystal, following Luttinger and Tisza's theory of dipole interaction.[4] They divided the lattice into $8p$ simple cubic sublattices ($p=1$ for S.C. lattice, $p=2$ for B.C.C. lattice and $p=4$ for F.C.C. lattice), where in each sublattice all dipoles are parallel, hence any state of dipole array should be represented by a point in $24p$ dimensional vector space. Under the condition that a vector representing any dipole array should be confined to the constant dipole surface $\sum_{i=1}^{8p} \sum_{\alpha=x}^{z} \mu_{i\alpha}^2 = const$, they reduced the problem of obtaining the dipole array with minimum energy to an eigen-value problem. That is, they looked for the array vector which is parallel to the dipolar field vector generated from the original array, and obtained the lowest array consistent with the condition $\sum_{\alpha=x}^{z} \mu_{i\alpha}^2 = \mu^2$, $i=1, \cdots, 8$. Here μ_α denotes the α-th component of dipole whose magnitude is equal to μ.

The quadrupole interaction takes a form (7) bilinear with respect to the five components of quadrupoles belonging to two interacting atoms (or molecules). A quadrupole localized at lattice point is considered as a vector whose components are given by

$$z_1 = \frac{\sqrt{3}}{2}(\xi^2 - \eta^2), \quad z_2 = \frac{1}{2}(2\zeta^2 - \xi^2 - \eta^2),$$

$$z_3 = \sqrt{3}\,\eta\zeta, \quad z_4 = \sqrt{3}\,\zeta\xi, \quad z_5 = \sqrt{3}\,\xi\eta. \tag{1}$$

Here ξ, η and ζ are Cartesian coordinates whose origin is at each lattice point. If we assume the vector (ξ, η, ζ) to be confined to the surface of the sphere with unit radius, the condition

$$\xi^2 + \eta^2 + \zeta^2 = 1 \tag{2}$$

leads to the condition

$$\sum_{i=1}^{5} z_i^2 = 1. \tag{3}$$

However, not all of z_i's are independent, because the components of a real quadrupole (1) are subjected only to two independent variables. Therefore a five-dimensional vector $\boldsymbol{z}(z_1, \cdots, z_5)$ subjected to (3) but free from (2) does not always correspond to a real quadrupole. But, in order to seek the quadrupole array of the lowest energy, we shall first solve our problem within a rather extended manifold of the fictitious quadrupole just mentioned. The procedure to be followed is in complete parallel with Luttinger and Tisza's method.

If the eigen-vector belonging to the lowest eigen-value represents a real quadrupole or if a linear combination of vectors which are degenerate to the lowest value represents a real quadrupole, that is all right. As we shall see later, however, in S.C. and B.C.C. lattices this is not the case and only in the F.C.C. lattice in which the actual problem is included we shall see such a situation to be realized.

There is a case in which the problem is greatly simplified. It appears in the quadrupole interaction between d-electrons in the e_g-state. Actually, if we represent the five components of a quadrupole by e_g-orbital:

$$\psi_1 = \frac{\sqrt{3}}{2}(\xi^2 - \eta^2), \quad \psi_2 = \frac{1}{2}(2\zeta^2 - \xi^2 - \eta^2), \tag{4}$$

we have

$$z_1 = -\frac{2}{7}\bar{r}^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad z_2 = -\frac{2}{7}\bar{r}^2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{5}$$

but the matrix components of z_3, z_4 and z_5 vanish identically, where $\bar{r}^2$ denotes averaged square of radius of electron coordinate. Using the Pauli spin matrix we may write them as

$$z_1 = -\frac{2}{7}\bar{r}^2 \sigma_x, \quad z_2 = -\frac{2}{7}\bar{r}^2 \sigma_z. \tag{6}$$

In this formalism, the procedure is very similar to that for the dipole array and

the exact classical solution is straightforwardly obtained for the three lattices considered.

§ 2. Quadrupole interaction

The quadrupole interaction between two quadrupoles is written in a usual form:

$$V_{q-q} = \frac{3e^2}{4R^5} r_1^2 r_2^2 f(\theta_1, \varphi_1; \theta_2, \varphi_2),\tag{7}$$

$$f(\theta_1, \varphi_1; \theta_2, \varphi_2) = 8P_2(\cos\theta_1)P_2(\cos\theta_2)$$

$$-16 \sin\theta_1 \cos\theta_1 \sin\theta_2 \cos\theta_2 \cos(\varphi_1-\varphi_2) + \sin^2\theta_1 \sin^2\theta_2 \cos 2(\varphi_1-\varphi_2).\tag{8}$$

Here $(r_i, \theta_i, \varphi_i)$ denote the polar coordinates of the position vector of electron whose origin is at the center of gravity of charge distribution localized around the i-th quadrupole, and the polar axis is taken to be a line connecting two centers of quadrupoles whose distance is equal to R (see Fig. 1).
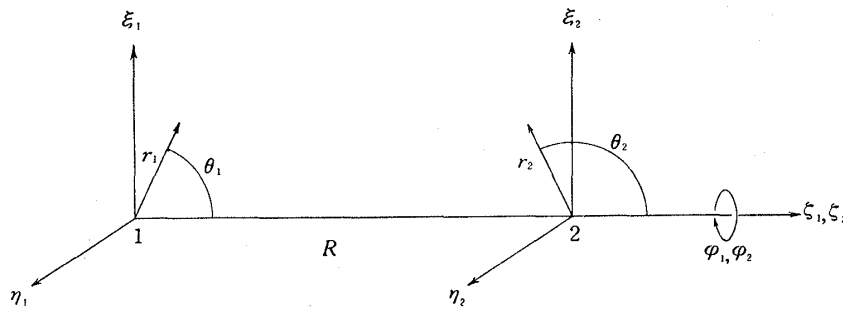

Fig. 1. The definitions of $(r_i, \theta_i, \varphi_i)$ and R.

If we take our coordinates system so as to coincide with three principal axes of cubic crystal, the quadrupole interaction (7) is transformed into

$$V_{q-q} = \frac{3}{4} e^2 \sum_{\mu,\nu=1}^{5} z_\mu(1) V_{\mu\nu}(R) z_\nu(2)\tag{9}$$

where $z_\mu(i)$ denotes the μ-th component of the i-th quadrupole and $V_{\mu\nu}(R)$'s are listed in Table I.

The next step is to construct a matrix of V_{q-q} with respect to the lowest degenerate states. The simplest case is concerned with doubly degenerate e_g-orbital (Γ_3 manifold in Bethe's notation), where (6) may be substituted for z.

In general cases, the matrix representation can be constructed with the help of operator equivalence method,[5] that is,

$$z_1 = c_J \frac{\sqrt{3}}{2}(J_x^2 - J_y^2), \quad z_2 = c_J \frac{1}{2} \cdot (2J_z^2 - J_x^2 - J_y^2),\cdots,\tag{10}$$

Table I.   Expressions for $V_{\mu\nu}(R) \times R^5$. (Θ, Φ) denote the polar angles of the direction R.

μ	ν	$P_4^0(\cos\Theta)$	$P_4^2(\cos\Theta)$		$P_4^4(\cos\Theta)$	
			$\cos 2\Phi$	$\sin 2\Phi$	$\cos 4\Phi$	$\sin 4\Phi$
1	1	2/3			1/36	
1	2		$1/3\sqrt{3}$			
1	5					1/36
2	2	4				
2	5			$1/3\sqrt{3}$		
3	3	−8/3	−2/9			
3	4			−2/9		
4	4	−8/3	2/9			
5	5	2/3				−1/36

μ	ν	$P_4^1(\cos\Theta)$		$P_4^3(\cos\Theta)$	
		$\cos\Phi$	$\sin\Phi$	$\cos 3\Phi$	$\sin 3\Phi$
1	3		1/3		1/18
1	4	−1/3		1/18	
2	3		$2/\sqrt{3}$		
2	4	$2/\sqrt{3}$			
3	5	−1/3		−1/18	
4	5		1/3		1/18

where c_J is dependent only on quantum number J of degenerate manifold. In these cases, the classical treatment of quadrupole interaction is to consider the energy (9) with quadrupole normalized in the sense of (3).

In such a way, the energy of the quadrupole interaction in crystal is written as

$$W = \sum_{j>k} \sum_{\mu,\nu} z_\mu^{\ j} F_{\mu\nu}(R_j - R_k) z_\nu^{\ k} \qquad (11)$$

in general cases, where $F_{\mu\nu}(R_j - R_k)$ is equal to $V_{\mu\nu}(R) \times (3e^2 \mu_Q^2/4)$ and z_μ is now the component of normalized quadrupole. In the following, we shall measure the quadrupole energy W in the units of $(3e^2\mu_Q^2/4a^5)$ where a denotes the lattice constant. $F_{\mu\nu}(R_j - R_k)$ are symmetric with respect to suffices μ and ν.

The physical meaning of $F_{\mu\nu}(R_j - R_k)$ is given by stating that the μ-th component of quadrupole field at the j-th lattice point is equal to $F_{\mu\nu}(R_j - R_k)$ if we put a unit fictitious quadrupole $z_\nu = 1$ at the k-th lattice point.

§ 3.   The e_g-orbital array in the S.C. lattice

Let us first study the array of fictitious spin associated with e_g-orbital in the S.C. lattice. The quadrupole energy (9) is then written as

$$W = \sum_{j>k} \sigma_j \cdot F(R_j - R_k) \cdot \sigma_k \qquad (12)$$

by substitution of (6) in (9), where the components of a dyadic $F(R)$ are given by

$$F_{xx}(R) = F_{11}(R), \quad F_{zx}(R) = F_{22}(R),$$
$$F_{xz}(R) = F_{zx}(R) = F_{12}(R), \qquad (13)$$

and the other components vanish identically.

We shall classically look for the lowest array of spin vector which is doubly periodic. Then we shall divide S.C. lattice into eight S.C. sublattices generated from eight lattice points:

$$(0\ 0\ 0), \quad (1\ 0\ 0), \quad (0\ 1\ 0), \quad (0\ 0\ 1),$$
$$(0\ 1\ 1), \quad (1\ 0\ 1), \quad (1\ 1\ 0) \text{ and } (1\ 1\ 1), \qquad (14)$$

in which all spins are parallel within each sublattice. Thus we have only to assign the spin orientation on the eight lattice points mentioned above in order to designate spin array in the crystal. If we assume a tentative array, it causes a field at, say, the k-th lattice point. Further, if the spin at this lattice point is parallel to the field generated there and the situation is the same in the whole lattice, the system will have a certain amount of efficient gain or loss of quadrupole energy. Following Luttinger and Tisza, we shall refer below to such array as characteristic array. The spin array with maximum gain or loss of quadrupole energy should naturally be included in the whole assembly of characteristic arrays.

Let us then find characteristic array Σ, which is designated by 2×8 components inclusive of eight spins because the y-component of σ disappears throughout eight sublattices. The characteristic array is thus obtained from an eigen-value problem:

$$F \cdot \Sigma = f \Sigma. \qquad (15)$$

Here the field operator F is a square matrix of sixteen dimension, whose component $F_{\mu\nu}^{pq}$, $p, q = 1, 2, \cdots, 8$; $\mu, \nu = 1, 2$ gives the μ-th component of the quadrupole field acting on a lattice point belonging to the p-th sublattice when we put spin along the ν-th direction on the q-th sublattice. Since the magnitude of Σ is given by

$$(\Sigma, \Sigma) = \sum_{i=1}^{8} (\sigma_i \cdot \sigma_i) = 8, \qquad (16)$$

the eigen-value of (15), f, just corresponds to twice as much as the quadrupole energy per atom, $1/16 \cdot (\Sigma, F \cdot \Sigma)$. Here the classical magnitude of fictitious spin is assumed to be equal to unity.

To obtain characteristic vector Σ, it is necessary to see the structure of field operator. It is a cyclic matrix with respect to p and q, whose component can be obtained with the help of Table I. Components $F_{\mu\nu}^{pp}$'s, $\mu, \nu = 1, 2$, are simply written as follows:

$$F_{11}^{pp} \equiv G_{11}(000) = \frac{1}{192} \cdot \sum_{\substack{l_1 l_2 l_3 \\ =-\infty}}^{\infty} [19(l_1^4+l_2^4)+4l_3^4-102\,l_1^2 l_2^2-12\,l_3^2(l_1^2+l_2^2)]/l^9,$$

$$F_{12}^{pp} \equiv G_{12}(000) = 5/64\sqrt{3} \cdot \sum_{\substack{l_1 l_2 l_3 \\ =-\infty}}^{\infty} (l_1^2-l_2^2)(6l_3^2-l_1^2-l_2^2)/l^9, \qquad (17)$$

$$F_{22}^{pp} \equiv G_{22}(000) = 1/64 \cdot \sum_{\substack{l_1 l_2 l_3 \\ =-\infty}}^{\infty} [3(l_1^4+l_2^4)+8l_3^4-24\,l_3^2(l_1^2+l_2^2)+6\,l_1^2 l_2^2]/l^9,$$

where $l^2=l_1^2+l_2^2+l_3^2$. The other components $F_{\mu\nu}^{pq}$, $p \neq q$, are also obtained from replacing l_1, l_2 and l_3 in (17) by $l_1-(u_1^p-u_1^q)/2$, $l_2-(u_2^p-u_2^q)/2$ and $l_3-(u_3^p-u_3^q)/2$ respectively, in which (u_1^p, u_2^p, u_3^p) denotes the lattice point generating the p-th S.C. sublattice as given by (14). According to this definition, we may put

$$F_{\mu\nu}^{pq} = G_{\mu\nu}\left(\frac{u_1^p-u_1^q}{2}, \frac{u_2^p-u_2^q}{2}, \frac{u_3^p-u_3^q}{2}\right), \qquad (18)$$

whose numerical values are tabulated in Table II (see the Appendix).

Table II. The numerical values of $G_{\mu\nu}(u_1 u_2 u_3)$.

u_1	u_2	u_3	$G_{11}(u)$	$G_{22}(u)$	$G_{12}(u)$
0	0	0	0.39	0.39	0
1/2	0	0	6.32	3.12	−2.77
0	1/2	0	6.32	3.12	2.77
0	0	1/2	1.52	7.91	0
0	1/2	1/2	0.29	−1.16	−1.26
1/2	0	1/2	0.29	−1.16	1.26
1/2	1/2	0	−1.88	1.02	0
1/2	1/2	1/2	−0.78	−0.78	0

The solution of an eigen-value equation (15) is much simplified if we make use of the cyclic nature of $F_{\mu\nu}^{pq}$. Without inquiring into the mathematical details, we see that the quadrupole field has the same translational symmetry as that of the spin array, hence the spin arrays of different symmetry cannot combine with each other. Taking this situation into account, let us construct a vector $\boldsymbol{\Sigma}_\mu(\boldsymbol{\lambda})$ by

$$\boldsymbol{\Sigma}_\mu(\boldsymbol{\lambda}) = \sum_{u^p} \exp(i\boldsymbol{\lambda} \cdot \boldsymbol{u}^p)\,\boldsymbol{e}_\mu^p \qquad (19)$$

where $\boldsymbol{e}_\mu^p$ refers to a unit vector which represents the p-th spin along the μ-th direction in which the other spins have zero component. Since there are 8×2 independent vectors $\boldsymbol{e}_\mu^p$, there are 8×2 independent $\boldsymbol{\Sigma}_\mu(\boldsymbol{\lambda})$, which we choose as

$$\boldsymbol{\lambda} = (0\ 0\ 0),\ (\pi\ 0\ 0),\ (0\ \pi\ 0),\ (0\ 0\ \pi),$$

$$(0\ \pi\ \pi),\ (\pi\ 0\ \pi),\ (\pi\ \pi\ 0)\ \text{and}\ (\pi\ \pi\ \pi). \qquad (20)$$

The basic arrays thus generated are shown in Fig. 2.

$$\lambda = \quad (000) \qquad (\pi 00) \qquad (0\pi 0) \qquad (00\pi)$$

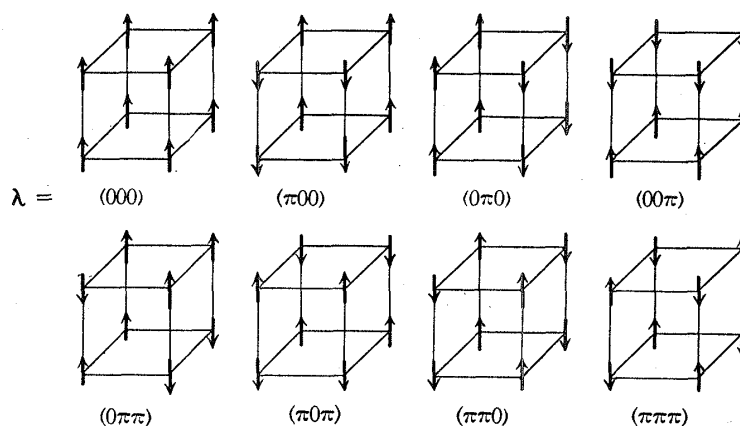$$(0\pi\pi) \qquad (\pi 0\pi) \qquad (\pi\pi 0) \qquad (\pi\pi\pi)$$

Fig. 2. Basic arrays for $\Sigma_z(\lambda)$.

In such a way, the eigen-value equation (15) becomes

$$F(\lambda) \cdot \Sigma(\lambda) = f \Sigma(\lambda). \tag{21}$$

Here $\Sigma(\lambda) = (\Sigma_x(\lambda), \Sigma_z(\lambda))$ and the components of $F(\lambda)$ are given by

$$F_{\mu\nu}(\lambda) = \sum_p G_{\mu\nu}\left(\frac{u_1^p}{2}, \frac{u_2^p}{2}, \frac{u_3^p}{2}\right) \exp(i\lambda \cdot u^p), \tag{22}$$

whose numerical values are obtained by the aid of Table II and given in Table III.

Due to the cubic symmetry of the lattice, it will be sufficient to search for the characteristic arrays with $\lambda = (0\ 0\ 0)$, $(0\ 0\ \pi)$, $(\pi\ \pi\ 0)$ and $(\pi\ \pi\ \pi)$, which are just given by $\Sigma_\mu(\lambda)$'s because Σ_x and Σ_z with those λ's do not combine with each other as can be seen in Table III. The lowest energy states can be realized by $\Sigma_x(\pi\ \pi\ 0)$, $\Sigma_z(\pi\ \pi\ \pi)$ and $\Sigma_x(\pi\ \pi\ \pi)$. The other arrays give essentially the same pattern.

Table III. The numerical values of $F_{\mu\nu}(\lambda)$.

$\lambda(\lambda_1\ \lambda_2\ \lambda_3)$	$F_{11}(\lambda)$	$F_{22}(\lambda)$	$F_{12}(\lambda)$
0 0 0	12.45	12.45 $(\equiv f_1)$	0
0 0 π	9.81 $(\equiv f_3)$	2.83 $(\equiv f_2)$	0
π π 0	-13.97 $(\equiv f_5)$	4.62 $(\equiv f_4)$	0
π π π	-14.28	-14.28 $(\equiv f_6)$	0

In order to derive the orbital array of e_g from the array of spin orientation, we may use the well-known spinor transformation. When the fictitious spin points the direction at angle θ from z-axis, the parallel and antiparallel states of spin along this direction are respectively transformed into

$$\psi_1{}' = \cos\frac{\theta}{2}\,\psi_1 + \sin\frac{\theta}{2}\,\psi_2,$$

$$\psi_2{}' = -\sin\frac{\theta}{2}\,\psi_1 + \cos\frac{\theta}{2}\,\psi_2, \tag{23}$$

in which ψ_1 and ψ_2 are doubly degenerate orbitals of e_g as given by (4). We shall discuss below the orbital array for respective cases mentioned above.

(i) $\boldsymbol{\lambda} = (0\ 0\ 0)$

This ferromagnetic solution corresponds to the uniform orbital array in which ψ_1(or ψ_2) is put on the whole lattice. Both solutions are degenerate with a high field value $f = 12.45$.

(ii) $\boldsymbol{\lambda} = (0\ 0\ \pi)$

We have the spin array in which spins are parallel among lattice points on the xy-plane but antiparallel between two adjacent xy-planes. An array with spin along the z-axis gives $f = 2.83$, while another array with spin along the x-axis gives a higher value $f = 9.87$. Both arrays have high energy.

(iii) $\boldsymbol{\lambda} = (\pi\ \pi\ 0)$

The field value is given by $f = 4.62$ or -13.97 according as spins are along the z- or x-axis. The spin array is such that the neighbouring spins along the z-axis are parallel but those along the x-axis and y-axis antiparallel. The orbital array with lower energy is obtained by putting

$$\psi_1{}' = \frac{1}{2\sqrt{2}}\,[\,(\sqrt{3}-1)\,\xi^2 - (\sqrt{3}+1)\,\eta^2 + 2\zeta^2\,],$$

$$\psi_2{}' = \frac{1}{2\sqrt{2}}\,[\,(\sqrt{3}+1)\,\xi^2 - (\sqrt{3}-1)\,\eta^2 - 2\zeta^2\,], \tag{24}$$
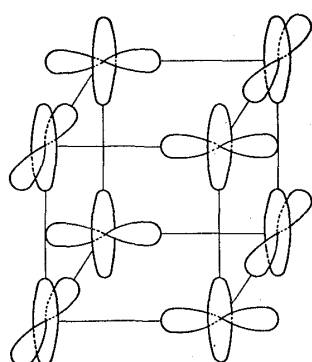
on the lattice, as can be seen in Fig. 3.
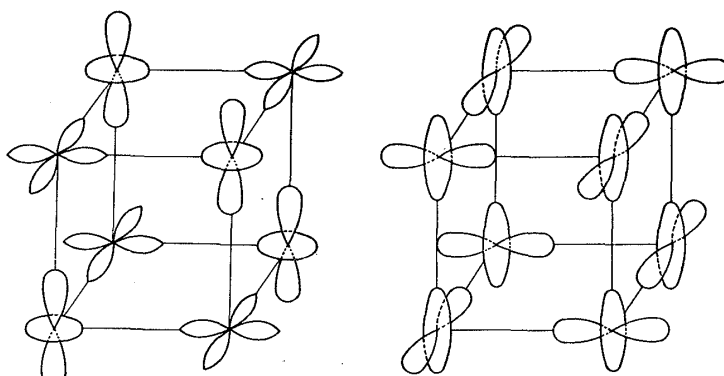

Fig. 3. Orbital array with $f = -13.97$.

(a)   (b)

Fig. 4. Orbital arrays being degenerate with $f = -14.28$.

(iv) $\boldsymbol{\lambda} = (\pi\ \pi\ \pi)$

Spins along the x- or z-axis are surrounded by antiparallel spins along the

same axis. Both arrays are degenerate with $f = -14.28$, whose orbital analogues are illustrated in Fig. 4.

§ 4. The e_g-orbital array in the B.C.C. and F.C.C. lattices

(A) *The e_g-orbital array in the B.C.C. lattice*

Dividing this lattice into S.C. sublattices, for each S.C. lattice we have the characteristic array, which are respectively designated by $\Sigma_\mu^1(\lambda)$ and $\Sigma_\mu^2(\lambda)$, in cases of $\lambda = (0\,0\,0)$, $(0\,0\,\pi)$, $(\pi\,\pi\,0)$ and $(\pi\,\pi\,\pi)$. In these cases, which are all worth knowing, characteristic arrays will be obtained within a subspace subtended by $\Sigma^1(\lambda)$ and $\Sigma^2(\lambda)$. In order to obtain these arrays, it will be necessary to know the quadrupole field on the 1st S.C. lattice coming from $\Sigma^2(\lambda)$. The μ-th component of the field is given by

$$F_{\mu\nu}^{12}(\lambda) \equiv \sum_{u^p} G_{\mu\nu}\left(\frac{1}{4} + \frac{u_1^p}{2}, \ \frac{1}{4} + \frac{u_2^p}{2}, \ \frac{1}{4} + \frac{u_3^p}{2}\right) \exp(i\lambda \cdot u^p), \quad (25)$$

which proves to vanish identically except a particular array with $\lambda = (0\,0\,0)$ because we have

$$G_{\mu\nu}\left(\frac{1}{4}, \ \frac{1}{4}, \ \frac{1}{4}\right) = G_{\mu\nu}\left(\frac{3}{4}, \ \frac{1}{4}, \ \frac{1}{4}\right) = \cdots, \quad (26)$$

for $\mu, \nu = 1, 2$. We can therefore see that there is no coupling between $\Sigma^1(\lambda)$ and $\Sigma^2(\lambda)$ in the case with $\lambda \neq 0$, in which the quadrupole energy per atom takes the same value as given in § 3.

Let us then consider the particular case $\lambda = (0\,0\,0)$. Using the following relations

$$G_{12}\left(\frac{1}{4}, \ \frac{1}{4}, \ \frac{1}{4}\right) = 0,$$

$$G_{11}\left(\frac{1}{4}, \ \frac{1}{4}, \ \frac{1}{4}\right) = G_{22}\left(\frac{1}{4}, \ \frac{1}{4}, \ \frac{1}{4}\right) = -3.10, \quad (27)$$

we have a field matrix

$$\begin{array}{c} \Sigma_\mu^1(0) \\ \Sigma_\mu^2(0) \end{array} \begin{bmatrix} f_1 & f_{11} \\ f_{11} & f_1 \end{bmatrix}, \quad (28)$$

where $f_1 = 12.45$ and $f_{11} = 8G_{11}(\frac{1}{4},\frac{1}{4},\frac{1}{4}) = -24.80$. Eigenvalues of the matrix are easily obtained as $f_1 \pm f_{11}$ equal to 37.25 or -12.35, which are higher in energy than f-values found in the array with $\lambda = (\pi\,\pi\,0)$ or $(\pi\,\pi\,\pi)$. From this analysis we find that in the lowest array of e_g-orbital there is no correlation between corner lattice and body-centered one in B.C.C. lattice.

(B) *The e_g-orbital array in the F.C.C. lattice*

The lattice is decomposed into four S.C. lattices, characterized by the following :

	corner	yz-face	zx-face	xy-face
generating point	(0 0 0)	(0 1/2 1/2)	(1/2 0 1/2)	(1/2 1/2 0)
label	1	2	3	4
characteristic array	$\Sigma^1(\lambda)$	$\Sigma^2(\lambda)$	$\Sigma^3(\lambda)$	$\Sigma^4(\lambda)$

In parallel with (25), we construct the field matrix. For example,

$$\sum_{u^p} G_{\mu\nu}\left(\frac{u_1^p}{2}, \frac{1}{4}+\frac{u_2^p}{2}, \frac{1}{4}+\frac{u_3^p}{2}\right)\exp\left(-i\lambda\cdot u^p\right) \qquad (29)$$

gives the matrix component between $\Sigma_\mu^1(\lambda)$ and $\Sigma_\nu^2(\lambda)$, which is denoted by $F_{\mu\nu}^{12}(\lambda)$.

A symmetric property,

$$F_{\mu\nu}^{12}(\lambda) = F_{\mu\nu}^{34}(\lambda), \quad F_{\mu\nu}^{13}(\lambda) = F_{\mu\nu}^{24}(\lambda),$$
$$F_{\mu\nu}^{14}(\lambda) = F_{\mu\nu}^{23}(\lambda), \qquad\qquad (30)$$

will be easily seen. The numerical values of $G_{\mu\nu}(u_1 u_2 u_3)$ necessary for our problem are tabulated in Table IV.

Table IV. Numerical values of $G_{\mu\nu}(u_1 u_2 u_3)$ necessary for the F.C.C. problem.

$(u_1 u_2 u_3)$	$G_{11}(u)$	$G_{22}(u)$	$G_{12}(u)$
0 1/4 1/4	2.96	−8.93	−10.30
1/2 1/4 1/4	−0.65	−0.42	0.20
1/4 1/4 0	−14.85	8.90	0
1/4 1/4 1/2	−0.30	−0.76	0

We shall now discuss the characteristic arrays with respective λ.

(i) $\lambda = (0\ 0\ 0)$

The field matrix is written in the following form:

$$
\begin{array}{c}
\Sigma_x^1 \\
\Sigma_x^2 \\
\Sigma_x^3 \\
\Sigma_x^4 \\
\Sigma_z^1 \\
\Sigma_z^2 \\
\Sigma_z^3 \\
\Sigma_z^4
\end{array}
\left(
\begin{array}{cccccccc}
f & a & a & b & 0 & e & -e & 0 \\
a & f & b & a & e & 0 & 0 & -e \\
a & b & f & a & -e & 0 & 0 & e \\
b & a & a & f & 0 & -e & e & 0 \\
0 & e & -e & 0 & f & c & c & d \\
e & 0 & 0 & -e & c & f & d & c \\
-e & 0 & 0 & e & c & d & f & c \\
0 & -e & e & 0 & d & c & c & f
\end{array}
\right). \qquad (31)
$$

In order to construct the characteristic array, we shall introduce the following four arrays:

$$[\Sigma_\mu{}^1, \quad \Sigma_\mu{}^2, \quad \Sigma_\mu{}^3, \quad \Sigma_\mu{}^4] \equiv S_\mu{}^1,$$

$$[\Sigma_\mu{}^1, \quad -\Sigma_\mu{}^2, \quad -\Sigma_\mu{}^3, \quad \Sigma_\mu{}^4] \equiv S_\mu{}^2,$$

$$[\Sigma_\mu{}^1, \quad -\Sigma_\mu{}^2, \quad \Sigma_\mu{}^3, \quad -\Sigma_\mu{}^4] \equiv S_\mu{}^3,$$

$$[\Sigma_\mu{}^1, \quad \Sigma_\mu{}^2, \quad -\Sigma_\mu{}^3, \quad -\Sigma_\mu{}^4] \equiv S_\mu{}^4.$$

(32)

Basing on these arrays, we may largely factorize the field matrix. We have

$$\begin{matrix} S_x{}^3 \\ S_z{}^3 \end{matrix} \begin{bmatrix} f_1-b & -2e \\ -2e & f_1-d \end{bmatrix}, \quad \begin{matrix} S_x{}^4 \\ S_z{}^4 \end{matrix} \begin{bmatrix} f_1-b & 2e \\ 2e & f_1-d \end{bmatrix}$$

(33)

and the other $S_\mu{}^p$'s give characteristic array, whose eigenvalue is found to be f_1+2a+b for $S_x{}^1$, f_1+2c+d for $S_z{}^1$, f_1-2a+b for $S_x{}^2$ and f_1-2c+d for $S_z{}^4$. If we use the numerical values $a=9.25$, $b=-60.60$, $c=-37.40$, $d=32.56$, $e=-40.40$ and $f\equiv f_1=12.45$, which are calculated with the help of Table IV and later referred to a, b, c, d and e as g_{11}, φ_{11}, g_{22}, φ_{22} and φ_{12} in the order, the lowest array proves to be given by $S_x{}^2$ with energy $f_1-2a+b=-66.65$. This lowest energy is three-fold degenerate, in which the other two arrays are included in S^3 and S^4 but these are crystallographically equivalent to $S_x{}^2$. The orbital analogue of array $S_x{}^2$ can be seen in Fig. 5.
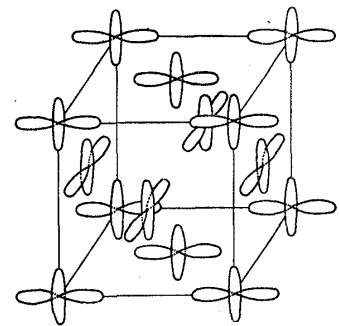

Fig. 5. The lowest orbital array in F. C. C. lattice.

(ii) $\lambda = (0\ 0\ \pi)$

The field matrix bringing the lowest energy is given by

$$\begin{matrix} \Sigma_x{}^1 \\ \Sigma_x{}^2 \end{matrix} \begin{bmatrix} f_3 & \varphi'_{11} \\ \varphi'_{11} & f_3 \end{bmatrix}$$

(34)

and another similar matrix concerned with $\Sigma_x{}^2$ and $\Sigma_x{}^3$. The lowest characteristic array is then given by a doubly degenerate set of $[\Sigma_x{}^1, \Sigma_x{}^2, \Sigma_x{}^3, \Sigma_x{}^4]$, and $[\Sigma_x{}^1, -\Sigma_x{}^2, -\Sigma_x{}^3, \Sigma_x{}^4]$ whose eigenvalue is equal to $f_3+\varphi'_{11}=-48.36$, since $\varphi'_{11}=-58.17$. In the other words, an xy-plane inclusive of lattice point of two sublattices 1 and 4 sit down cannot be correlated with adjacent xy-planes inclusive of those of sublattices 2 and 3 sit down.

(iii) $\lambda = (\pi\ \pi\ 0)$, $(\pi\ \pi\ \pi)$

In these cases, there is no coupling between different sublattices. The lowest value is given by $f_6=-14.28$.

The characteristic array with the lowest energy is then included in $\lambda = (0\ 0\ 0)$. It may be concluded that in F.C.C. lattice an energy gain due to the interaction between sublattices is much larger than a loss due to the self-energy. On the other hand, in B.C.C. lattice it is not the case.

§ 5. The quadrupole array in the S.C. lattice

If we consider a quadrupole as a fictitious vector of five dimensions, Z, nor-

malized in the sense of (3), the procedure for obtaining the quadrupole array is straightforward.

Let us now generalize the matrix component of field operator, $F_{\mu\nu}^{pq}$, given by (18), to the general quadrupole with $\mu, \nu = 1, \cdots, 5$. The new components of $F_{\mu\nu}^{pq}$ are also defined by $G_{\mu\nu}((u^p - u^q)/2)$. These are obtained with the help of Table I. Writing them formally in a simple case, we have

$$G_{13}(0\ 0\ 0) = \frac{5}{96} \sum_{\substack{l_1 l_2 l_3 \\ =-\infty}}^{\infty} l_2 l_3 (9 l_1^2 - 5 l_2^2 + 2 l_3^2)/l^9,$$

$$G_{15}(0\ 0\ 0) = \frac{35}{96} \sum_{\substack{l_1 l_2 l_3 \\ =-\infty}}^{\infty} l_1 l_2 (l_1^2 - l_2^2)/l^9,$$

$$G_{23}(0\ 0\ 0) = \frac{5}{32\sqrt{3}} \sum_{\substack{l_1 l_2 l_3 \\ =-\infty}}^{\infty} l_2 l_3 (4 l_3^2 - 3 l_1^2 - 3 l_2^2)/l^9, \qquad (35)$$

$$G_{25}(0\ 0\ 0) = -\frac{5}{32\sqrt{3}} \sum_{\substack{l_1 l_2 l_3 \\ =-\infty}}^{\infty} l_1 l_2 (6 l_3^2 - l_1^2 - l_2^2)/l^9,$$

$$G_{33}(0\ 0\ 0) = \frac{2}{96} \sum_{\substack{l_1 l_2 l_3 \\ =-\infty}}^{\infty} [l_1^4 - 4(l_2^4 + l_3^4) - 3 l_1^2 (l_2^2 + l_3^2) + 27 l_2^2 l_3^2]/l^9.$$

General expression for $G_{\mu\nu}(\boldsymbol{u})$ is derived from the above expression by substituting $l_1 - u_1$, $l_2 - u_2$ and $l_3 - u_3$ for l_1, l_2 and l_3 respectively.

The other $G_{\mu\nu}(\boldsymbol{u})$'s are the following:

$$G_{14}(u_1 u_2 u_3) = G_{13}(u_2 u_1 u_3),$$

$$G_{24}(u_1 u_2 u_3) = G_{23}(u_2 u_1 u_3),$$

$$G_{33}(u_1 u_2 u_3) = G_{44}(u_2 u_1 u_3) = G_{55}(u_3 u_2 u_1), \qquad (36)$$

$$G_{34}(u_1 u_2 u_3) = G_{35}(u_1 u_3 u_2) = G_{45}(u_2 u_1 u_3) = -\frac{2\sqrt{3}}{3} G_{25}(u_1 u_2 u_3).$$

In S.C. lattice, $z_\mu^p (\mu = 3, 4, 5)$, designating the array of fictitious quadrupole of z_μ put on the p-th sublattice, does not couple with the other components of quadrupole, as can easily be seen from inspection of (35). Characteristic array is therefore obtained as

$$\boldsymbol{Z}_\mu(\boldsymbol{\lambda}) = \sum_{\boldsymbol{u}^p} \exp(i\boldsymbol{\lambda} \cdot \boldsymbol{u}^p) z_\mu^p;$$

$$\mu = 3, 4, 5, \qquad (37)$$

where z_μ^p denotes a vector analogous to e_μ^p in (19). The corresponding eigenvalue of the field is given by $F_{\mu\mu}(\boldsymbol{\lambda})$ of (22), which in turn is obtained from $G_{\mu\mu}(\boldsymbol{u})$. The value for $G_{\mu\mu}(\boldsymbol{u})$ for $\mu = 3, 4, 5$ can be derived from $G_{\mu\nu}(\boldsymbol{u})$ for $\mu, \nu = 1, 2$ (Appendix), and $F_{\mu\mu}(\boldsymbol{\lambda})$'s thus estimated are tabulated in Table V. The other components of field matrix are essentially given by those in Table III.

Thus, the lowest energy of fictitious quadrupole proves to be given by $Z_1(\pi\,\pi\,\pi)$ and $Z_2(\pi\,\pi\,\pi)$ or almost by $Z_1(\pi\,\pi\,0)$, whose eigenvalue $f_6 = -14.28$ or $f_5 = -13.97$ is considerably lower than -8.87 associated with $Z_5(0\,0\,\pi)$. But, these characteristic arrays are all fictitious, because they are not consistent with (1) on the surface of unit sphere.

Although we treat the quadrupole as a fictitious vector, whole assembly of characteristic arrays obtained forms a complete set, whence any array of real quadrupole with double periodicity can be constructed by a linear combination. Let an array of real quadrupole be Z:

$$Z = \sum_{j,\lambda} a_{j\lambda} Z_j(\lambda),\tag{38}$$

where $\sum |a_{j\lambda}|^2 = 1$. The energy, $1/2 \cdot f$, associated with this array is then obtained by

$$f = \sum_{j,\lambda} |a_{j\lambda}|^2 f_j(\lambda),\tag{39}$$

where $f_j(\lambda)$ denotes the eigenvalue of F belonging to $Z_j(\lambda)$. This relation can be easily proved with the help of

$$f = (1/8)(Z, FZ).$$

Table V. The numerical values of $F_{\mu\mu}(\lambda)$ for $\mu = 3$, 4 and 5. The other values omitted can be obtained from appropriate cyclic permutation.

$\lambda_1\,\lambda_2\,\lambda_3$	$F_{33}(\lambda)$	$F_{44}(\lambda)$	$F_{55}(\lambda)$
0 0 0	-8.30	-8.30	-8.30
0 0 π	-1.88	-1.88	-8.87
$\pi\,\pi\,0$	-3.08	-3.08	15.51
$\pi\,\pi\,\pi$	9.52	9.52	9.52

Due to the cubic symmetry, a real quadrupole will probably be parallel to one of (0 0 1), (1 1 0), (1 1 1) and the other cubically equivalent directions in the lowest state. The real quadrupole parallel to (0 0 1) is simply represented by $z_2 = 1$ and $z_1 = z_3 = z_4 = z_5 = 0$, which proves to correspond to $\zeta = 1$ and $\xi = \eta = 0$ if we use (1). It may be noted that $z_2 = -1$ with $z_1 = z_3 = z_4 = z_5 = 0$ is a fictitious quadrupole. If we take new coordinate system (ξ', η', ζ') whose ζ'-axis is parallel to (1 1 0), the real quadrupole with $z_2' = 1$ and $z_1' = z_3' = z_4' = z_5' = 0$ is also parallel to (1 1 0), where z''s denote the quadrupole components in the new coordinate system. Using the transformation formula $\zeta' = 1/\sqrt{2} \cdot (\xi + \eta)$, we have

$$z_2' = -\left(\frac{1}{2}z_2 + \frac{\sqrt{3}}{2}z_5\right).$$

In the same way, the real quadrupole parallel to (1 1 1) proves to be represented by the state in which

$$z_2'' = 1/\sqrt{3} \cdot (z_3 + z_4 + z_5) = 1$$

and all of the other z_j'''s are equal to zero where z_j'''s denote the quadrupole components in the coordinate system with ζ''-axis parallel to $(1\ 1\ 1)$. The real quadrupole parallel to one of the other three equivalent directions: $(-1\ 1\ 1)$, $(1\ -1\ 1)$ and $(1\ 1\ -1)$ is represented by the state in which one of

$$\frac{1}{\sqrt{3}}(z_3 - z_4 - z_5), \quad \frac{1}{\sqrt{3}}(-z_3 + z_4 - z_5) \quad \text{and} \quad \frac{1}{\sqrt{3}}(-z_3 - z_4 + z_5)$$

is equal to unity where the other four independent components of quadrupole can always make zero.

In such manner, we construct array of real quadrupole and examine the field value associated. Some results with lower energy are given in Table VI, whose patterns can be seen in Fig. 6.

Table VI. Some arrays of real quadrupole in S. C. lattice.

array	field value	figure 6
$(1/\sqrt{3})\,[\boldsymbol{Z}_3(0\ 0\ 0) + \boldsymbol{Z}_4(0\ 0\ 0) + \boldsymbol{Z}_5(0\ 0\ 0)]$;	-8.30	(a)
$(1/\sqrt{3})\,[\boldsymbol{Z}_3(\pi\ 0\ 0) + \boldsymbol{Z}_4(\pi\ 0\ 0) + \boldsymbol{Z}_5(0\ 0\ 0)]$;	-6.35	(b)
$-\,[(1/2)\cdot\boldsymbol{Z}_2(0\ 0\ 0) + (\sqrt{3}/2)\cdot\boldsymbol{Z}_5(0\ 0\ \pi)]$;	-3.56	(c)
$-\,[(\sqrt{3}/2)\cdot\boldsymbol{Z}_1(\pi\ \pi\ 0) + (1/2)\cdot\boldsymbol{Z}_2(0\ 0\ 0)]$;	-7.37	(d)

(a) (b) (c) (d)
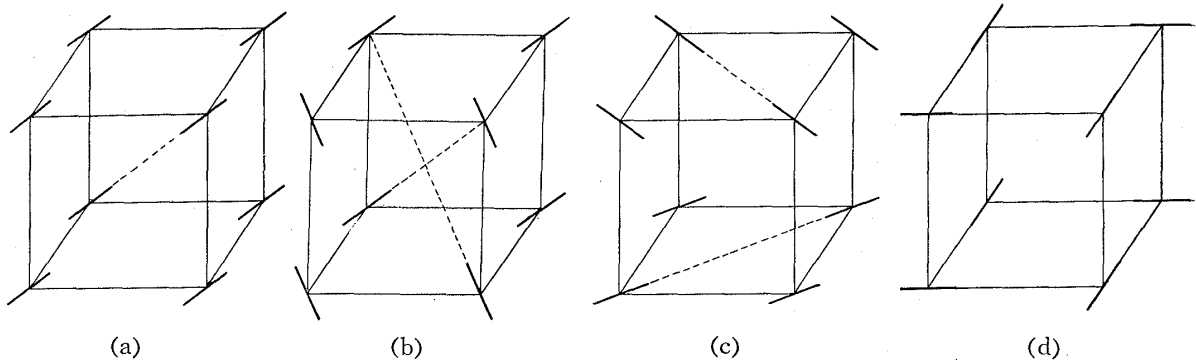
Fig. 6. Quadrupole arrays given in Table VI.

The lowest array will be $(1/\sqrt{3}) \cdot (\boldsymbol{Z}_3 + \boldsymbol{Z}_4 + \boldsymbol{Z}_5)$ with $\lambda = (0\ 0\ 0)$, an array in which all quadrupoles are directed along a trigonal axis of S.C. crystal. Of course, there are four arrays of such type, corresponding to four trigonal axes of cubic crystal.

§ 6. The quadrupole array in the B.C.C. and F.C.C. lattices

The procedure is somewhat similar to that in S.C. lattice, and we may decompose B.C.C. or F.C.C. lattice into two or four S.C. sublattices and construct

the field matrix with respect to S.C. characteristic arrays of fictitious quadrupole, as can be seen in Table VIII. The numerical values are obtained from $G_{\mu\nu}(u)$'s whose independent quantities are tabulated in Table VII. The other $G_{\mu\nu}(u)$'s can be derived from relations given in the Appendix.

We shall below discuss the quadrupole array in B.C.C. and F.C.C. lattices separately by use of the field matrix given in Table VIII.

(A) *Quadrupole array in B.C.C. lattice*

As can be seen in Table VII, two S.C. characteristic arrays with $\lambda = (0\ 0\ \pi)$

Table VII. Numerical values of $G_{\mu\nu}(u)$.

$u_1\ u_2\ u_3$	$G_{33}(u)$	$G_{13}(u)$
1/4 1/4 1/4	2.07	2.36
1/4 1/4 0	−5.93	0
1/4 1/4 1/2	0.51	0
0 1/4 1/4	17.84	−6.00
1/2 1/4 1/4	0.05	0.87

Table VIII A. Quadrupole field at body-, yz face-, zx face- and xy face-centered points, coming from a characteristic array on the corner lattice.

λ	array	field at B. C. pt.	field at F. C. pt. yz-face	zx-face	xy-face
(0 0 0)	Z_1	$f_{11}Z_1$	$g_{11}Z_1 + g_{12}Z_2$	$h_{11}Z_1 + h_{12}Z_2$	$\varphi_{11}Z_1$
	Z_2	$f_{22}Z_2$	$g_{22}Z_2 + g_{21}Z_1$	$h_{22}Z_2 + h_{21}Z_1$	$\varphi_{22}Z_2$
	Z_3	$f_{33}Z_3$	$g_{33}Z_3$	$h_{33}Z_3$	$\varphi_{33}Z_3$
	Z_4	$f_{44}Z_4$	$g_{44}Z_4$	$h_{44}Z_4$	$\varphi_{44}Z_4$
	Z_5	$f_{55}Z_5$	$g_{55}Z_5$	$h_{55}Z_5$	$\varphi_{55}Z_5$
(0 0 π)	Z_1				$\varphi_{11}'Z_1$
	Z_2				$\varphi_{22}'Z_2$
	Z_3				$\varphi_{33}'Z_3$
	Z_4				$\varphi_{44}'Z_4$
	Z_5				$\varphi_{55}'Z_5$
(π π 0)	Z_1				
	Z_2	$f_{25}Z_5$			$\varphi_{25}Z_5$
	Z_3	$f_{34}Z_4$			$\varphi_{34}Z_4$
	Z_4	$f_{43}Z_3$			$\varphi_{43}Z_3$
	Z_5	$f_{52}Z_2$			$\varphi_{52}Z_2$
(π π π)	Z_1		$g_{13}Z_3$	$h_{14}Z_4$	
	Z_2		$g_{23}Z_3$	$h_{24}Z_4$	$\varphi_{25}'Z_5$
	Z_3		$g_{31}Z_1 + g_{32}Z_2$	$h_{35}Z_5$	$\varphi_{34}'Z_4$
	Z_4		$g_{45}Z_5$	$h_{41}Z_1 + h_{42}Z_2$	$\varphi_{43}'Z_3$
	Z_5		$g_{54}Z_4$	$h_{53}Z_3$	$\phi_{52}'Z_2$

Table VIII B.   Numerical values for the matrix component.

component	value	component	value
f_{11}, f_{22}	-24.81	φ_{11}'	-58.17
f_{33}, f_{44}, f_{55}	16.54	φ_{22}'	38.66
f_{25}	-21.82	φ_{33}', φ_{44}'	-25.78
f_{34}	25.19	φ_{55}'	70.56
g_{11}, h_{11}	9.25	φ_{25}	24.02
g_{22}, h_{22}	-37.40	φ_{34}	-27.70
g_{12}, $-h_{12}$	-40.40		
g_{33}, h_{44}, φ_{55}	72.19	g_{13}, $-h_{14}$	-27.36
g_{44}, h_{33}, φ_{33}		g_{23}, h_{24}, $1/2 \cdot \varphi_{25}'$	15.79
g_{55}, h_{55}, φ_{44}	-21.70	g_{45}, h_{35}, φ_{34}'	-36.40
φ_{11}	-60.60		
φ_{22}	32.56		

and $(\pi\,\pi\,\pi)$ do not couple with each other, hence the energy value is given by a self-energy of S.C. characteristic array.   It will be sufficient to look into the arrays with $\lambda = (0\ 0\ 0)$ and $(\pi\,\pi\,0)$.

   (i) $\lambda = (0\ 0\ 0)$

Field matrix is very similar to (28).   The characteristic arrays and their field values are as follows:

$$[\boldsymbol{Z}_1,\ \boldsymbol{Z}_1],\ [\boldsymbol{Z}_2,\ \boldsymbol{Z}_2]: \qquad\qquad f = -12.35,$$

$$[\boldsymbol{Z}_1,\ -\boldsymbol{Z}_1],\ [\boldsymbol{Z}_2,\ -\boldsymbol{Z}_2]: \qquad\qquad 37.25,$$

$$[\boldsymbol{Z}_3,\ \boldsymbol{Z}_3],\ [\boldsymbol{Z}_4,\ \boldsymbol{Z}_4],\ [\boldsymbol{Z}_5,\ \boldsymbol{Z}_5]: \qquad 8.23, \qquad\qquad (40)$$

$$[\boldsymbol{Z}_3,\ -\boldsymbol{Z}_3],\ [\boldsymbol{Z}_4,\ -\boldsymbol{Z}_4],\ [\boldsymbol{Z}_5,\ -\boldsymbol{Z}_5]: \qquad -24.8.$$

$[\boldsymbol{Z}_2,\ \boldsymbol{Z}_2]$ gives real quadrupole (Fig. 7a), but the other characteristic arrays are fictitious.   By use of their linear combination, we shall look for the array of real quadrupole.

$$-(\sqrt{3}/2 \cdot [\boldsymbol{Z}_5,\ -\boldsymbol{Z}_5] + 1/2 \cdot [\boldsymbol{Z}_2,\ \boldsymbol{Z}_2]) \qquad\qquad (41)$$

is a real quadrupole, which has field value equal to -21.7 and will be the lowest in B.C.C. lattice (Fig. 7b).

Another real quadrupole array which gives rather low field value -13.8 is constructed as

$$1/\sqrt{3} \cdot ([\boldsymbol{Z}_3,\ -\boldsymbol{Z}_3] + [\boldsymbol{Z}_4,\ -\boldsymbol{Z}_4] + [\boldsymbol{Z}_5,\ \boldsymbol{Z}_5]), \qquad\qquad (42)$$

which can be seen in Fig. 7c.

   (ii) $\lambda = (\pi\,\pi\,0)$

Fictitious arrays of lower field value are

$$[\mathbf{Z}_1, \ \mathbf{Z}_1], \ [\mathbf{Z}_1, \ -\mathbf{Z}_1]: \qquad f = -14.2,$$

$$[\mathbf{Z}_3, \ -\mathbf{Z}_4], \ [\mathbf{Z}_4, \ -\mathbf{Z}_3]: \qquad -28.3. \tag{43}$$

A real quadrupole array constructed from them is

$$1/\sqrt{3} \, ([\mathbf{Z}_3, \ -\mathbf{Z}_4] + [\mathbf{Z}_4, \ -\mathbf{Z}_3]) \quad (\pi \, \pi \, 0)$$

$$+ 1/\sqrt{3} \, [\mathbf{Z}_5, \ \mathbf{Z}_5] \quad (0 \ 0 \ 0), \tag{44}$$

whose field value is found to be -16.1. This array is illustrated in Fig. 7d.

(a)　　　　　　(b)　　　　　　(c)　　　　　　(d)
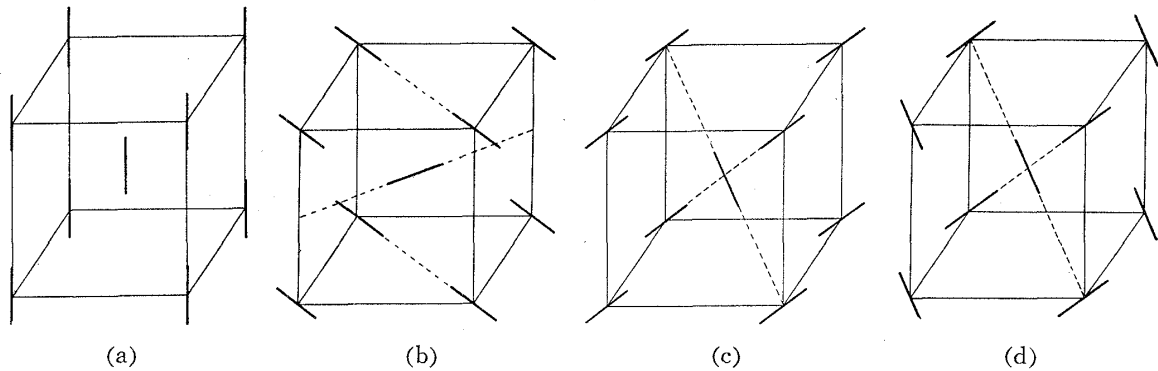
Fig. 7. Quadrupole arrays in B.C.C. lattice

(B)　*Quadrupole array in F.C.C. lattice*

(i)　$\boldsymbol{\lambda} = (0 \ 0 \ 0)$

While $\mathbf{Z}_1$ and $\mathbf{Z}_2$ couple with each other, each of $\mathbf{Z}_3$, $\mathbf{Z}_4$ and $\mathbf{Z}_5$ does not couple with any different type of $\mathbf{Z}_j$ respectively. The characteristic arrays have a similar form to (32). For example,

$$[\mathbf{Z}_3, \quad \mathbf{Z}_3, \quad \mathbf{Z}_3, \quad \mathbf{Z}_3], : \quad f = 20.5,$$

$$[\mathbf{Z}_3, \quad -\mathbf{Z}_3, \quad -\mathbf{Z}_3, \quad \mathbf{Z}_3], : \quad -80.5,$$

$$[\mathbf{Z}_3, \quad -\mathbf{Z}_3, \quad \mathbf{Z}_3, \quad -\mathbf{Z}_3], : \quad -80.5, \tag{45}$$

$$[\mathbf{Z}_3, \quad \mathbf{Z}_3, \quad -\mathbf{Z}_3, \quad -\mathbf{Z}_3], : \quad 107.3.$$

In such a way, we may find the lowest array of two-fold degeneracy from respective $\mathbf{Z}_i$, $i=1, 2$ and 3. Then we designate them by

$$\mathbf{X}_1 = [\mathbf{Z}_3, \quad -\mathbf{Z}_3, \quad -\mathbf{Z}_3, \quad \mathbf{Z}_3],$$

$$\mathbf{X}_2 = [\mathbf{Z}_4, \quad \mathbf{Z}_4, \quad -\mathbf{Z}_4, \quad -\mathbf{Z}_4], \tag{46}$$

$$\mathbf{X}_3 = [\mathbf{Z}_5, \quad -\mathbf{Z}_5, \quad \mathbf{Z}_5, \quad -\mathbf{Z}_5],$$

$$\mathbf{Y}_1 = [\mathbf{Z}_3, \quad -\mathbf{Z}_3, \quad \mathbf{Z}_3, \quad -\mathbf{Z}_3],$$

$$\mathbf{Y}_2 = [\mathbf{Z}_4, \quad -\mathbf{Z}_4, \quad -\mathbf{Z}_4, \quad \mathbf{Z}_4], \tag{47}$$

$$\mathbf{Y}_3 = [\mathbf{Z}_5, \quad \mathbf{Z}_5, \quad -\mathbf{Z}_5, \quad -\mathbf{Z}_5].$$

We can construct real quadrupole arrays by using this degenerate set. They are designated by

$$1/\sqrt{3}\,(X_1+X_2+X_3),\quad 1/\sqrt{3}\,(Y_1+Y_2+Y_3),\qquad (48)$$

whose field value is of course equal to -80.5. This array can be seen in Fig. 8. On the other hand, the lowest characteristic array constructed by Z_1 and Z_2 has been obtained in § 4 (B). This array, being now fictitious, has brought a field value equal to -66.65, but any real quadrupole array constructed by using it is of higher energy.

(ii) $\lambda = (0\ 0\ \pi)$

The lowest arrays are

$$[Z_5,\ -Z_5,\ -Z_5,\ Z_5],\ [Z_5,\ -Z_5,\ Z_5,\ -Z_5],$$

Fig. 8. The lowest quadrupole array in F. C. C. lattice.

whose field value is found to be -79.4. Each of them should be combined with the other characteristic array with higher energy in order to construct any real array, resulting in a promotion of energy. Some field values of array are given by -48.4, -37.4, -27.7, etc.

(iii) $\lambda = (\pi\ \pi\ 0),\ (\pi\ \pi\ \pi)$

Field values are given by $(-60.7,\ -50.3,\ -14.0,\ 25.2,\ 66.5)$ for $(\pi\ \pi\ 0)$ and $(-37.6,\ -12.8,\ 3.6,\ 26.2,\ 27.7)$ for $(\pi\ \pi\ \pi)$, which are of no interest.

We may finally conclude that the array (48) leads to the exact lowest field value in F.C.C. lattice, which is considerably lower than the corresponding value in § 4 (B).

§ 7.   Quadrupole interaction in magnetic compounds and molecular crystals

(A)   *The orbital ordering of localized magnetic electron*

Although the quadrupole interaction is not very effective, our result seems to give some insights into the preferential ordering of d-orbitals which are two-fold (e_g) or three-fold (t_{2g}) degenerate under a crystalline field of cubic symmetry.

Let us first look into the stabilizing character of t_{2g}-orbital in S.C., B.C.C. and F.C.C. lattices. Since we have done the corresponding study about e_g-orbital in §§ 3 and 4, we may then compare the results for both types of orbital. Three orbitals of t_{2g} are written as

$$\phi_1 = \sqrt{3}\,\eta\zeta,\quad \phi_2 = \sqrt{3}\,\zeta\xi,\quad \phi_3 = \sqrt{3}\,\xi\eta.\qquad (49)$$

By using them, the quadrupole components are represented by (10) with $c_J = -\frac{2}{7}\cdot\overline{r^2}$, where J_x, J_y and J_z should be understood to be the components of orbital angular momentum with quantum number equal to unity. An oriented quadrupole corresponds to a state in which z_2 has the maximum magnitude along the orientation
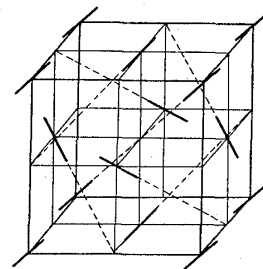
axis, say, the z-axis, hence a state with the eigenvalue of J_z equal to zero. Since z_2 equals -1 in this state, the classical treatment of the t_{2g}-problem is just given by that in §§ 5 and 6 with the same magnitude of quadrupole moment, $\mu_Q(=-\frac{2}{7}\cdot\bar{r}^2)$, as in the e_g-problem.

In such a way, we shall compare the ordering energy of t_{2g}-orbital, which the results obtained in §§ 5 and 6 give, with that of e_g-orbital obtained in §§ 3 and 4. We shall recapitulate the results for respective lattice in Table IX. As can be seen in this table, the quadrupole energy associated with e_g is much stabilized in S.C. lattice than that with t_{2g}, but the situation is reversed in B.C.C. and F.C.C. lattices.

As mentioned in § 1, the ordering of e_g-orbital plays the important role in order to understand the magnetic structure of $LaMnO_3$ and MnF_3. In these compounds, the magnetic lattice is essentially S.C., where an orbital pattern Fig. 4(b)

Table IX. The lowest array for e_g- and t_{2g}-orbitals.

orbital		S. C.	B. C. C.	F. C. C.
e_g	array	Fig. 4	Fig. 4	Fig. 5
	field value	-14.28	-14.28	-66.5
t_{2g}	array	Fig. 6 (a)	Fig. 7 (b)	Fig. 8
	field value	-8.30	-21.7	-80.5

seems to be realized. The reason why the pattern which the compounds mentioned choose is not the type of Fig. 4(a) but that of Fig. 4(b) should be interpreted in terms of a certain kind of the Jahn-Teller distortion. In actuality, the field value for $LaMnO_3$ proves to be about 200°K in unit of the Boltzmann constant, hence the excitation energy necessary to reverse a fictitious spin is estimated to be about 400°K. It is rather small compared with the observed transition temperature $\sim$780°K, where the e_g-orbital ordering is considered to melt. But we will not further inquire into this problem in the present paper.

We shall here note another point. Any pattern which is not constructed by one of the lowest patterns or linear combination of them will always be higher in quadrupole energy. For example, we shall discuss the energy associated with an orbital array as shown in Fig. 9(a), where two non-orthogonal orbitals,

$$1/2\cdot(2\xi^2-\eta^2-\zeta^2),\quad 1/2\cdot(2\eta^2-\xi^2-\zeta^2),\quad\quad\quad(50)$$

are mounted on lattice points as shown. These orbitals will be written as

$$\frac{\sqrt{3}}{2}\psi_1-\frac{1}{2}\psi_2,\quad-\frac{\sqrt{3}}{2}\psi_1-\frac{1}{2}\psi_2.\quad\quad\quad(51)$$

Comparing (51) with (23), we shall obtain the spin pattern in which two kinds of spins, pointing the directions at angles $-\pi/3$ and $\pi/3$ from the z-axis in the zx-plane, align alternatively in lattice (Fig. 9(b)). This array may be con-

sidered as a superposition of two arrays, in which one is an array with ferromagnetic spin along the z-axis and another with antiferromagnetic array, $\boldsymbol{\lambda} = (\pi\,\pi\,\pi)$, of spin along the x-axis. The coefficients of linear combination proves to be $1/2$ and $\sqrt{3}/2$ for respective array. Therefore we obtain the corresponding field value as

$$[(\sqrt{3}/2)^2(-14.28) + (1/2)^2 \cdot (12 \cdot 45)] = -7.60$$

with the help of (39) and Table III.

(B) *The orientational ordering in molecular crystal*

We shall discuss some aspects of crystal structure observed in molecular crystal. Although our results are to be applied to molecular crystals composed of molecules with large quadrupole moment in cubic crystal, we shall also refer further to crystals of the other types.[6]

(i) *B.C.C. lattice*

The lowest pattern is of the type Fig. 7 (b), which will be supposed to be distorted tetragonally. Such crystal structure is found in fluorides and oxides of metals, which is ionic crystal and is well-known as rutile or SnO_2-type structure.
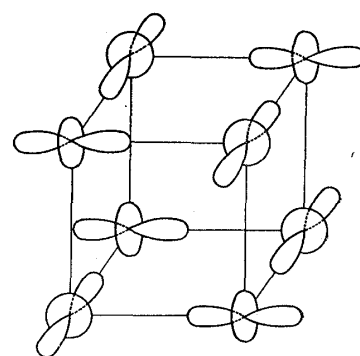
Another pattern of the type Fig. 7 (a), being rather low in energy, is found in hydrogen cyanide HCN, which is distorted tetragonally.[7] Since this

(a)

(b)

Fig. 9. An orbital array (a) and its spin analogue (b).

molecule has large electrical dipole moment ($\mu = 2.65 \times 10^{-18}$ e.s.u.),[8] our prediction of crystal structure fails naturally. But quadrupole moment of HCN is also large ($\mu_Q = 0.775 \times 10^{-16}$ cm^2).[9]
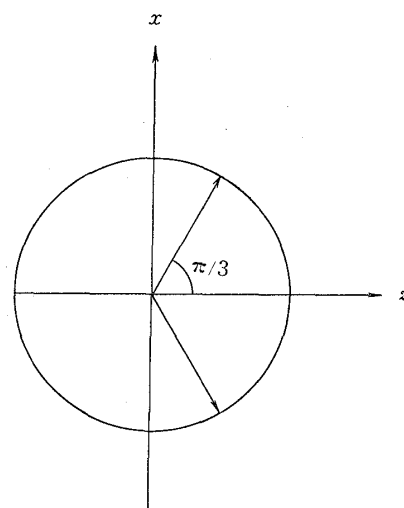
(ii) *F.C.C. lattice*

Some molecular crystals composed of non-polar molecules with appreciable magnitude of quadrupole moment are known and are listed in Table X. The quadrupole energy per molecule, W_Q, is estimated as one half of the field value, -80.5, multiplied by $3e^2\mu_Q^2/4a^5$. In these crystals listed, crystal lattice is of the same structure at low temperatures, which is just the lowest pattern predicted in Fig. 8. We shall note some features observed for respective crystals.

Nitrogen (N_2).[10] The orientational ordering breaks down at transition point 34.5°K, which is comparable with the quadrupole energy per molecule in unit of the Boltzmann constant k.

Nitric oxide (N_2O). N_2O molecule is of the form N–N–O, hence probably has very small dipole moment. Due to its large quadrupole moment, the quadru-

Table X. Lattice constant (a), transition temperature (T_λ), melting point (T_M), quadrupole moment (μ_Q) and quadrupole energy per molecule (W_Q) of molecular crystals of solid nitrogen type crystallized in F.C.C. lattice.[13],[14]

molecular crystal	$a \times 10^8$ cm	$T_\lambda °$K	$T_M °$K	$\mu_Q \times 10^{16}$ cm²	$W_Q °$K
N_2	5.56	34.5	63.08	0.155	20
N_2O	5.66		182.3	0.455	127
CO_2	5.58		190	0.32	94
CO	5.63	64.55	68.1	0.165	24

pole energy is comparable with kT of melting temperature. We suppose that this will be one of the reasons why the orientational order persists up to the melting point in this crystal.

Carbon dioxide (CO_2).[11] CO_2 molecule is of the form O–C–O, hence without dipole moment. The situation will be similar to that in nitric oxide.

Carbon monoxide (CO).[12] CO molecule has small dipole moment $\mu = 0.1 \times 10^{-18}$ e.s.u.[8] and therefore we suppose that quadrupole effect is much more effective than dipole effect in solid state. The transition point of CO crystal is, however, higher than that of N_2 crystal. This will probably be due to dipole-quadrupole interaction between CO molecules.

Another interesting feature observed for N_2O and CO crystals is that there remains a further disorder concerned with such direction as N–N–O or C–O within the pattern of nitrogen type at very low temperatures. This is supposed to be due to the situation that their directions are determined by small dipolar effect.

Acknowledgement

Appendix

Some relations between $G_{\mu\nu}(u)$'s

The following symmetries can be easily established by inspecting (17) : $G_{\mu\mu}(u_1 u_2 u_3)$'s are symmetric with respect to permutation between u_1 and u_2, while $G_{12}(u_1 u_2 u_3)$ is antisymmetric with respect to the same permutation. And we can see further relations :

$$G_{11}(u_1 u_2 u_3) + G_{11}(u_2 u_1 u_3) + G_{11}(u_3 u_1 u_2)$$

$$= G_{22}(u_1 u_2 u_3) + G_{22}(u_2 u_3 u_1) + G_{22}(u_3 u_1 u_2),$$

$$G_{11}(u_1 u_2 u_3) - G_{11}(u_3 u_2 u_1) = G_{22}(u_3 u_2 u_1) - G_{22}(u_1 u_2 u_3),$$

$$G_{12}(vuu) = \sqrt{3}/4 \cdot [G_{22}(uuv) - G_{11}(uuv)].$$

(A·1)

Using these relations, we can derive G_{12} and G_{22} from G_{11}, for example,

$$G_{22}(uuv) = 1/3 \cdot [4G_{11}(vuu) - G_{11}(uuv)],$$

$$G_{22}(vuu) = 1/3 \cdot [G_{11}(vuu) + 2G_{11}(uuv)].$$

(A·2)

We shall note some useful relations for $G_{\mu\nu}$'s, μ, $\nu = 1, \cdots, 5$. If we compare G_{33}, of (35) with $G_{\mu\nu}$ of (17), a relation

$$G_{33}(u_1 u_2 u_3) = -\frac{2}{3} G_{22}(u_1 u_2 u_3) - \frac{2}{\sqrt{3}} G_{12}(u_1 u_2 u_3)$$

(A·3)

is established, hence G_{33}, G_{44} and G_{55}, can be derived from G_{11}, G_{22} and G_{12} with the help of (36). Other relations are as follows:

$$G_{23}(vuu) = 1/2 \cdot G_{25}(uuv) = -1/\sqrt{3} \cdot G_{13}(vuu),$$

$$G_{34}(uuv) = 4/3 \cdot G_{21}(vuu),$$

(A·4)

$$G_{33}(uuv) = G_{33}(uvu) = -2/3 \cdot G_{11}(uuv),$$

which are obtained in the same way.

References

1) T. Nakamura, Prog. Theor. Phys. **14** (1955), 135.
2) J. Kanamori, Prog. Theor. Phys. **17** (1957), 177.
3) E. O. Wollan and W. C. Koehler, Phys. Rev. **100** (1955), 545.
   E. O. Wollan, H. R. Child, W. C. Koehler and M. K. Wilkinson, Phys. Rev. **112** (1958), 1132.
   J. B. Goodenough, Phys. Rev. **100** (1955), 564.
4) J. M. Luttinger and L. Tisza, Phys. Rev. **70** (1946), 954.
5) K. W. H. Stevens, Proc. Phys. Soc. A **65** (1952), 209.
6) R. W. G. Wyckoff, *Crystal Structure* (Inter Science Publishers, Inc., New York, 1948).
7) W. J. Dumage and W. N. Lipscomb, Acta Cryst. **4** (1951), 330.
8) P. Debye, *Polar Molecules* (Chemical Catalog Co., New York, 1929).
9) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).
10) L. Vegard, Z. Physik **58** (1929), 497.
11) J. de Smedt and W. H. Keesom, Proc. Acad. Sci. Amsterdam **27** (1924), 839.
12) L. Vegard, Z. Physik **61** (1930), 185.
13) K. Clusius, Z. physik. Chem. B **3** (1929), 41.
14) J. O. Cloyton and W. F. Giauque, J. Am. Chem. Soc. **54** (1942), 2610.