in superconductivity seem to be of such a strength and range as to satisfy this condition. Although the derivation is valid only for the ground state (at $T=0$), we can safely assert that thermal excitations at sufficiently low temperatures will have a negligible effect on these results. It thus seems that, as far as the strength and range of the interaction are concerned, the application of the Tomonaga model in Ref. 5 is justified.

In conclusion, we point out that the core $[-n^*, n^*]$ is not completely filled, and it is an open and interesting question to estimate the effect of a few holes present in the core.

ACKNOWLEDGMENT

The authors are grateful to Professor F. Bloch for many helpful discussions.

APPENDIX

The quantity C is defined in Eq. (3.40) by the asymptotic behavior of the function $Q(r)$ for large r:

$$Q(r) \xrightarrow[r\to\infty]{} 2\sinh^2\theta(0)\ln r + C + O(1/r^2). \quad (A1)$$

It is convenient to rewrite $Q(r)$, given in Eq. (3.38), as

$$Q(r) = \int_0^\infty \lambda(k)(1-\cos kr)k^{-1}dk, \quad (A2)$$

where

$$\lambda(k) \equiv 2\sinh^2\theta(k). \quad (A3)$$

Using the relationship

$$\int_0^\infty k^{-1}(\cos k - \cos kr)dk = \ln r$$

and Eq. (A3), Eq. (A2) may be written

$$Q(r) = 2\sinh^2\theta(0)\ln r + \int_0^\infty [\lambda(k) - \lambda(0)\cos k]k^{-1}dk - T(r), \quad (A4)$$

where

$$T(r) = \int_0^\infty k^{-1}[\lambda(k) - \lambda(0)]\cos kr dk.$$

Integrating by parts twice, we find

$$T(r) \to O(1/r^2) \quad (A5)$$

for large r. Combining Eqs. (A4) and (A5) and comparing with Eq. (A1), we obtain

$$C = \int_0^\infty k^{-1}[\lambda(k) - \lambda(0)\cos k]dk.$$

Using Eq. (A3) to express this in terms of $\theta(k)$, one obtains Eq. (3.45) of the text.

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Elementary Excitations in fcc Solid Ortho-Hydrogen

J. C. Raich
Department of Physics, Colorado State University, Fort Collins, Colorado
AND
Richard D. Etters
Douglas Advanced Research Laboratories, Huntington Beach, California

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An equation-of-motion formalism is used to give a nonlinear spin-wave treatment of fcc solid ortho-hydrogen. The elementary excitations in ortho-hydrogen are librational waves and can be treated in a manner similar to spin waves in magnetism. The excitation spectrum, long-range order, and ground-state energy are calculated. It is found that the spin-wave excitations have a nonvanishing effect on both the long-range order and the ground-state energy. But, because of a large energy gap, the spin-wave-theory results deviate only slightly from their molecular-field values.

I. INTRODUCTION

THE cooperative orientational ordering of ortho-H_2 molecules on a rigid fcc lattice has been described in terms of a molecular-field approximation by Raich and James.[1,2] This treatment was based on a knowledge of the molecular equilibrium orientations, as found from the ground state of a system of classical quadrupoles on

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[1] J. C. Raich and H. M. James, Phys. Rev. Letters **16**, 173 (1966).

[2] H. M. James and J. C. Raich, Phys. Rev. **126**, 649 (1967).

a rigid fcc lattice,[3,4] and experiment.[5–8] Miyagi and Nakamura[9] have recently estimated the corrections to the ground-state energy for ortho-H_2 molecules on fcc and hcp lattices due to a spin-wave type zero-point energy. This effect was studied by considering rotational excitations in the ordered state, similar to spin-waves in antiferromagnets, where there is also a correction to the ground state as a result of the nonvanishing of a zero-point energy. Miyagi and Nakamura used a second-order perturbation treatment of this correction.

The method of temperature-dependent Green's functions has been applied to the above molecular-field model of ortho-hydrogen.[10] It was found that this problem can be solved by methods very similar to those used in the theories of ferro- and antiferromagnetism. It therefore seems reasonable to apply approximations, other than the molecular-field treatment, which are useful there, to the ortho-H_2 problem. One such method commonly used in magnetism is the spin-wave approximation. The application of a linear spin-wave theory, valid only at very low temperatures, has in fact been outlined by Homma, Okada, and Matsuda.[11] They calculate the energies of the low-lying excitations and an approximate density of the excited states in solid ortho-H_2. These excitations can be considered librational waves or "spin-waves."

The purpose of this paper is to give a nonlinear spin-wave treatment of solid ortho-H_2 for the fcc case using an equation-of-motion formalism developed by Wallace.[12] The method used is an application of the theory of Wallace including degenerate perturbation theory. The present work can in a way be considered an extension of the calculations of Homma *et al.*,[11] to finite temperatures. However, the methods used here are different. The excitation operators developed in this paper differ from those of Homma *et al.*, in that they are boson operators only at zero temperature.

During the preparation of this article we received another paper by Ueyama and Matsubara,[13] in which the authors also use a Green's-function technique to calculate the ground-state configuration, the low-lying excitations, and the temperature dependence of long-range order. The results obtained there however differ from those of the present work. Ueyama and Matsubara find no significant deviation from the molecular-field theory results. It is shown that, using the treatment described here, one finds indeed a small, but nonzero, deviation of the long-range order and other quantities from their molecular-field values.

Section II gives a description of the Hamiltonian for the model to be considered. Here we have chosen to use the angular momentum operators J^+, J^-, and J^z instead of the operators J^x, J^y, and J^z. This choice leads us to a somewhat different formalism than the one used by Miyagi and Nakamura[9] and others.[11,13] In Sec. III, the creation and annihilation operators of the system are defined. An outline of the linear spin-wave approximation is given in Sec. IV. The results of the linear spin-wave calculations are then used in Sec. V as a guide to the nonlinear spin-wave problem. Here the equations of motion are developed and solved for the proper excitation operators and excitation energies of the system. Section VI gives an outline of the calculation of the temperature dependence of the long-range order. An estimate of the ground-state energy is given in Sec. VII. The conclusions drawn from the present treatment are given in Sec. VIII.

II. HAMILTONIAN

The details of the model to be considered here are described adequately in the literature.[1,2,9] The Hamiltonian for a system of H_2 molecules in the rotational state $J=1$, coupled by quadrupole-quadrupole interactions is

$$H=\tfrac{1}{2}\sum_{ij}V_{ij}(\mathbf{\Omega}_i,\,\mathbf{\Omega}_j),\qquad(2.1)$$

where $\mathbf{\Omega}_i=(\theta_i,\phi_i)$ specifies the orientation of a molecule on site i relative to the crystal axis. V_{ij} is the quadrupole-quadrupole interaction[1,2]

$$V_{ij}=(20\pi/9)(70\pi)^{1/2}\Gamma_{ij}\sum_{MN}C(224;MN)\times Y_{2M}(\mathbf{\Omega}_i)Y_{2N}(\mathbf{\Omega}_j)Y_{4,M+N}(\mathbf{\Omega}_{ij})^*.\qquad(2.2)$$

Here $C(J_1J_2J;M_1M_2)$ is a Clebsch-Gordan coefficient[14] and

$$\Gamma_i=6e^2Q^2/(25R_{ij}^5),\qquad(2.3)$$

where Q is the molecular-quadrupole moment, (see footnote 27 of Ref. 2 on the value of Q), and $\mathbf{R}_{ij}$ is the vector connecting sites i and j, measured relative to the crystal axis.

The molecular lattice for solid ortho-H_2 is found to consist of four simple cubic sublattices,[1–4,10] with molecular-equilibrium directions oriented along the four different threefold axes of the crystal. The threefold axes coincide with the body diagonals of the fcc lattice. These equilibrium directions are the axes of quantization for each sublattice. For the present discussion it is

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therefore more convenient to transform to a coordinate system where the z_i axis, for each molecule i, is along the symmetry axis for that molecule i. This transformation is[14]

$$Y_{2M}(\mathbf{\Omega}_i)=\sum_m D^2{}_{Mm}{}^*(\alpha_i,\beta_i,\gamma_i)\,Y_{2m}(\boldsymbol{\omega}_i), \tag{2.4}$$

where $D^2{}_{Mm}$ is a rotation matrix, α_i, β_i, and γ_i are the Euler angles specifying the orientation of the equilibrium axis for molecule i (or axis of quantization for molecule i) relative to the crystal axis, and $\boldsymbol{\omega}_i=(\vartheta_i,\varphi_i)$ describes the orientation of molecule in i relative to its equilibrium axis.

In the subspace of $J=1$ one can then replace the spherical harmonics $Y_{2m}(\boldsymbol{\omega}_i)$ by their operator equivalents[15]

$$Y_{2m}(\boldsymbol{\omega}_i)=A_m\mathcal{O}_i{}^m, \tag{2.5}$$

where

$$\begin{aligned}A_0&=-\tfrac{1}{5}(5/4\pi)^{1/2},\\ A_{\pm1}&=\pm\tfrac{1}{10}(15/2\pi)^{1/2},\\ A_{\pm2}&=-\tfrac{1}{10}(15/2\pi)^{1/2},\end{aligned} \tag{2.6}$$

and

$$\begin{aligned}\mathcal{O}_i{}^0&=3(J_1{}^z)^2-2,\\ \mathcal{O}_i{}^{\pm1}&=J_i{}^zJ_i{}^{\pm}+J_i{}^{\pm}J_i{}^z,\\ \mathcal{O}_i{}^{\pm2}&=(J_i{}^{\pm})^2.\end{aligned} \tag{2.7}$$

Units where $\hbar=1$ are used throughout. The Hamiltonian (1) can be written in operator form

$$H=\sum_{ij}\sum_{mn}\gamma_{ij}{}^{mn}\mathcal{O}_i{}^m\mathcal{O}_j{}^n, \tag{2.8}$$

where

$$\gamma_{ij}{}^{mn}=(10\pi/9)(70\pi)^{1/2}\Gamma_{ij}A_mA_n\sum_{MN}C(224;MN)\times Y_{4,M+N}(\mathbf{\Omega}_{ij})^*D^2{}_{Mm}{}^*(\alpha_i,\beta_i,\gamma_i)\,D^2{}_{Nn}{}^*(\alpha_j,\beta_j,\gamma_j). \tag{2.9}$$

The relationship between this Hamiltonian and the one used by Nagai and Nakamura[3] and others[9,11,13] is given in Appendix A. Here $\mathbf{J}_i$ is the angular momentum operator for an H$_2$ molecule on site i, with the z_i axis taken along the equilibrium orientation of that molecule i. The components of $\mathbf{J}_i$ satisfy the usual commutation relations

$$[J_i{}^+,J_j{}^-]=2J_i{}^z\delta_{ij},\qquad [J_i{}^{\pm},J_j{}^z]=\mp J_i{}^{\pm}\delta_{ij}, \tag{2.10}$$

where the brackets indicate commutators, and

$$J_j{}^{\pm}=J_j{}^x\pm iJ_j{}^y. \tag{2.11}$$

For $J=1$ the relations

$$J_i{}^{\pm}J_j{}^z=\pm J_j{}^{\pm}J_j{}^z \tag{2.12}$$

hold. In this paper we consider only nearest-neighbor interactions, that is

$$\begin{aligned}\Gamma_{ij}&=\Gamma, &&\text{if } i \text{ and } j \text{ are nearest-neighbor sites}\\ &=0, &&\text{otherwise.}\end{aligned} \tag{2.13}$$

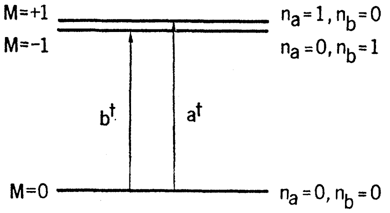

FIG. 1. Schematic illustration of the creation operators $a^\dagger$ and $b^\dagger$.

III. CREATION AND ANNIHILATION OPERATORS

One knows from the molecular-field approximation that the rotational states of the system can be described by molecular wave functions that have the form $Y_{1M}(\boldsymbol{\omega}_i)$, with $M=0$, ±1, in the coordinate system where the molecular orientations are described by $\boldsymbol{\omega}_i$. In the molecular-field treatment one finds that the states $M=\pm1$ are degenerate for a fcc lattice, but not for a hcp lattice,[9] and lie above the $M=0$ ground state. We are thus looking for operators that when applied to the state $M=0$ will create excitations in either the state $M=+1$ or the state $M=-1$.

Clearly the operators J^+ and J^-, given by Eq. (2.11), will not do. For example, J^+ operating on the state $M=-1$ gives a state of lower energy, i.e., the state $M=0$. Thus, for this problem, J^+ can not be considered a pure creation operator for $M=+1$ excitations. This is not even true in an approximate sense, contrasting with the theory of ferromagnetism. A set of operators that have the properties of annihilation operators are

$$a_i=(1/\sqrt{2})[1-(J_i{}^z)^2]J_i{}^-, \tag{3.1}$$

$$b_i=(1/\sqrt{2})[1-(J_i{}^z)^2]J_i{}^+, \tag{3.2}$$

with the creation operators $a_i{}^\dagger$ and $b_i{}^\dagger$ given by the Hermitian conjugates of Eqs. (3.1) and (3.2). It is easy to show that these operators satisfy the following commutation relations:

$$[a_i,a_j{}^\dagger]=(1-2n_{ai}-n_{bi})\delta_{ij}, \tag{3.3}$$

$$[b_i,b_j{}^\dagger]=(1-n_{ai}-2n_{bi})\delta_{ij}, \tag{3.4}$$

$$[a_i,b_j{}^\dagger]=-b_i{}^\dagger a_i\delta_{ij}, \tag{3.5}$$

$$[b_i,a_j{}^\dagger]=-a_i{}^\dagger b_i\delta_{ij}, \tag{3.6}$$

$$[a_i,b_j]=[a_i{}^\dagger,b_j{}^\dagger]=0, \tag{3.7}$$

where $n_{ai}=a_i{}^\dagger a_i$ and $n_{bi}=b_i{}^\dagger b_i$ are the number of $M=+1$ and $M=-1$ excitations, respectively, for site i. A schematic of these operators is given in Fig. 1.

The transformations (3.1) and (3.2) can be inverted

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[15] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **14**, 135 (1955).

to give

$$J_i^z = a_i^\dagger a_i - b_i^\dagger b_i, \tag{3.8}$$

$$J_i^+ = \sqrt{2}(a_i^\dagger + b_i), \tag{3.9}$$

$$J_i^- = \sqrt{2}(a_i + b_i^\dagger), \tag{3.10}$$

and

$$(J_i^z)^2 = a_i^\dagger a_i + b_i^\dagger b_i, \tag{3.11}$$

so that

$$\mathcal{O}_i^0 = 3(a_i^\dagger a_i + b_i^\dagger b_i) - 2 \tag{3.12}$$

$$\mathcal{O}_i^{+1} = \sqrt{2}(a_i^\dagger - b_i), \qquad \mathcal{O}_i^{-1} = (\mathcal{O}_i^{+1})^\dagger, \tag{3.13}$$

$$\mathcal{O}_i^{+2} = 2a_i^\dagger b_i, \qquad \mathcal{O}_i^{-2} = (\mathcal{O}_i^{+2})^\dagger. \tag{3.14}$$

One should note here that the operators $a^\dagger$ and $b^\dagger$ differ from the operators $x^\dagger$ and $y^\dagger$ introduced by Homma *et al.*[11] The commutation relations (3.3) through (3.7) show that the operators specified by Eqs. (3.8), (3.9), and (3.10) are not boson operators. However, at zero temperature, the two formalisms should coincide.

Using Eqs. (3.12), (3.13), and (3.14) the Hamiltonian (2.8) is written in terms of the operators a_i, $b_i^\dagger$, $a_i^\dagger$ and $b_i^\dagger$. The result is

$$\begin{aligned} H = \sum_{ij} \{ & \gamma_{ij}^{00}[3(n_{ai}+n_{bi})-2][3(n_{aj}+n_{bj})-2] \\ & +2[\gamma_{ij}^{+1+1}(a_i^\dagger - b_i)(a_j^\dagger - b_j) \\ & +\gamma_{ij}^{+1-1}(a_i^\dagger - b_i)(a_j - b_j^\dagger) + \text{H.c.}] \\ & +4[\gamma_{ij}^{+2+2}a_i^\dagger b_i a_j^\dagger b_j + \gamma_{ij}^{+2-2}a_i^\dagger b_i b_j^\dagger a_j + \text{H.c.}] \\ & +6\sqrt{2}[\gamma_{ij}^{+10}(a_i^\dagger - b_i)(n_{aj}+n_{bj}) - \text{H.c.}] \\ & +12[\gamma_{ij}^{+20}a_i^\dagger b_i(n_{aj}+n_{bj}) + \text{H.c.}] \\ & +4\sqrt{2}[\gamma_{ij}^{+2+1}a_i^\dagger b_i(a_j^\dagger - b_j) \\ & +\gamma_{ij}^{+2-1}a_i^\dagger b_i(a_j - b_j^\dagger) - \text{H.c.}]\}, \end{aligned} \tag{3.15}$$

where H.c. means Hermitian conjugate. Here we have used the relations

$$\gamma_{ij}^{-m,-n} = (-1)^{m+n}\gamma_{ij}^{mn*}, \tag{3.16}$$

$$\gamma_{ij}^{mn} = \gamma_{ji}^{nm}, \tag{3.17}$$

$$\sum_j \gamma_{ij}^{m0} = 0, \qquad m \neq 0, \tag{3.18}$$

which follow from the definition of $\gamma_i{}^{mn}$, Eq. (2.9).

One also has to keep in mind that the operators a_i, b_i, $a_i^\dagger$, and $b_i^\dagger$ are operators within the $J=1$ subspace, so that, for example,

$$a_i a_i = b_i b_i = a_i^\dagger a_i^\dagger = b_i^\dagger b_i^\dagger = a_i b_i = a_i^\dagger b_i^\dagger = 0.$$

The procedure used here is to give a description of the system by calculating the equations of motion for the operators a_i and b_i, using the Hamiltonian (3.15). These equations of motion are then used to derive the excitation spectrum and the thermodynamic averages of interest.

IV. LINEAR SPIN-WAVE APPROXIMATION

A. Effective Hamiltonian

At very low temperatures nearly all molecules must be in the ground state specified by $M=0$. Since n_a and n_b represent the number of $M=+1$ and $M=-1$ excitations, respectively, we should expect that the statistical averages $\langle n_a \rangle$ and $\langle n_b \rangle$ should be small at low temperatures. Or alternatively, denoting the ground state by $|0\rangle$, one finds from Eq. (3.3) that

$$[a_i, a_j^\dagger]|0\rangle = \delta_{ij}|0\rangle. \tag{4.1}$$

Thus, at low temperatures the spin-wave operators for ortho-H_2 can be defined in a manner similar to the Bloch spin waves in ferromagnetism. Therefore, near $T=0$ we may replace the commutation relations (3.3) through (3.7) by the approximate ones

$$[a_i, a_j^\dagger] = [b_i, b_j^\dagger] = \delta_{ij}, \tag{4.2}$$

$$[a_i, b_j^\dagger] = [b_i, a_j^\dagger] = [a_j, b_j] = [a_i^\dagger, b_j^\dagger] = 0. \tag{4.3}$$

Similarly, for excitations near $T=0$, one may neglect all but bilinear terms in the operators a, b, $a^\dagger$, and $b^\dagger$ in the Hamiltonian (3.15). The linear spin-wave Hamiltonian is then

$$\begin{aligned} H = 2\sum_{ij} \{ & \gamma_{ij}^{00}[1 - 3(a_j^\dagger a_j + b_j^\dagger b_j)] \\ & +\gamma_{ij}^{+1-1}(a_i^\dagger - b_i)(a_j - b_j^\dagger) \\ & +\gamma_{ij}^{+1+1}(a_i^\dagger - b_i)(a_j^\dagger - b_j)\} + \text{H.c.} \end{aligned} \tag{4.4}$$

Here the terms containing a coefficient γ_{ij}^{mn} with $m \neq 0$ and $n=0$ vanish because of Eq. (3.18). Those with $m=\pm 1$, $n=\pm 2$ and $m=\pm 2$, $n=\pm 1$ contain only trilinear terms, while those with $m=\pm 2$, $n=\pm 2$ contain quadrilinear terms. Both latter terms are neglected in a linear spin-wave treatment.

Since a description of the elementary excitations in solid ortho-H_2 at $T=0$ has already been outlined,[9,11] we will restrict our attention to only a first-order perturbation treatment of the linear spin-wave approximation. The first-order treatment, although somewhat simpler than the exact treatment, does not yield the zero-point energy of the spin-wave excitations. A calculation of this zero-point energy requires a second-order perturbation treatment.[9] The first-order treatment is included here primarily as an illustration of the techniques that will be used in the more exact nonlinear spin-wave approximation. The latter calculations should of course yield the correct zero-temperature results.

For a first-order perturbation treatment we need to retain only the diagonal terms plus only those terms leading to a degeneracy in the Hamiltonian (4.4). The remaining terms can then be treated by higher-order perturbation theory. The alternative procedure, which is used in Sec. V is to diagonalize the complete problem. For the first-order treatment we thus keep only those terms in Eq. (4.4) that connect states with equal zero-order energies, for example, terms like $a_i^\dagger a_i$, $a_i^\dagger a_j$, or $a_i^\dagger b_j$. Terms like $a_i^\dagger a_j^\dagger$ or $a_i^\dagger b_j^\dagger$ are neglected to first order, since they give nonvanishing contributions only between states with different zero-order energies.

B. Equations of Motion

To first order the equations of motion are then, from Eqs. (3.17) and (4.2)–(4.4)

$$[a_i, H]=19\Gamma a_i+4\sum_j(\gamma_{ij}{}^{+1-1}a_j-\gamma_{ij}{}^{+1+1}b_j), \tag{4.5}$$

$$[b_j, H]=19\Gamma b_j+4\sum_j(-\gamma_{ij}{}^{+1-1*}a_j+\gamma_{ij}{}^{+1+1*}b_j), \tag{4.6}$$

where we have used the relation $\gamma_{ij}{}^{00}=-(19/144)\Gamma$,[10] and the nearest-neighbor approximation (2.13). The equations of motion for the operators $a_i^\dagger$ and $b_i^\dagger$ are found by taking the Hermitian conjugates of Eqs. (4.5) and (4.6). An examination of the equations of motion shows that to first order the excitations a_i on the site i are coupled to excitations a_j and b_j for different sites j. A higher-order treatment will also mix in $a_j^\dagger$ and $b_j^\dagger$ as seen in Sec. V. Equations (4.5) and (4.6) are simplified in the usual manner by a Fourier transformation. Here one defines the operators

$$a_\alpha(\mathbf{k})=\surd(4/N)\sum_{j(\alpha)}\exp[i\mathbf{k}\cdot\mathbf{j}(\alpha)]a_{j(\alpha)}, \tag{4.7}$$

$$b_\alpha(\mathbf{k})=\surd(4/N)\sum_{j(\alpha)}\exp[i\mathbf{k}\cdot\mathbf{j}(\alpha)]b_{j(\alpha)}, \tag{4.8}$$

where α is the sublattice index, $\alpha=1, 2, 3, 4$, $\mathbf{k}$ is a vector in reciprocal space, and N is the total number of sites in the system. The sums are over all sites j on a given sublattice α. In terms of the Fourier-transformed operators (4.7) and (4.8) the equations of motion (4.5) and (4.6) are

$$[a_\alpha(\mathbf{k}), H]=19\Gamma a_\alpha(\mathbf{k})\\ +4\sum_\beta[\gamma_{\alpha\beta}{}^{+1-1}(\mathbf{k})a_\beta(\mathbf{k})-\gamma_{\alpha\beta}{}^{+1+1}b_\beta(\mathbf{k})], \tag{4.9}$$

$$[b_\alpha(\mathbf{k}), H]=19\Gamma b_\alpha(\mathbf{k})\\ +4\sum_\beta[-\gamma_{\alpha\beta}{}^{+1-1*}(\mathbf{k})a_\beta(\mathbf{k})+\gamma_{\alpha\beta}{}^{+1+1*}(\mathbf{k})b_\beta(\mathbf{k})], \tag{4.10}$$

where

$$\gamma_{\alpha\beta}{}^{mn}(\mathbf{k})=\gamma_{\alpha\beta}{}^{mn}(-\mathbf{k})\\ =\sum_{j(\beta)}\gamma_{i(\alpha)j(\beta)}{}^{mn}\exp\{-i\mathbf{k}\cdot[\mathbf{j}(\beta)-\mathbf{i}(\alpha)]\}. \tag{4.11}$$

It is seen from Eqs. (4.9) and (4.10) that the elementary excitations of the system are mixtures of a_α and b_α type excitations for $\alpha=1, 2, 3, 4$.

Let us define the operators $c_\mu(\mathbf{k})$, $\mu=1, 2\cdots 8$, by the vector

$$\begin{bmatrix} c_1(\mathbf{k}) \\ c_2(\mathbf{k}) \\ \cdot \\ \cdot \\ \cdot \\ c_8(\mathbf{k}) \end{bmatrix} = \begin{bmatrix} a_1(\mathbf{k}) \\ a_2(\mathbf{k}) \\ \cdot \\ \cdot \\ \cdot \\ b_4(\mathbf{k}) \end{bmatrix}, \tag{4.12}$$

and the 8×8 matrix $F(\mathbf{k})$, with matrix elements $F_{\mu\nu}$, $\mu, \nu=1, 2\cdots 8$

$$F(\mathbf{k})=\begin{bmatrix} f(\mathbf{k}) & -g(\mathbf{k}) \\ -g^*(\mathbf{k}) & f^*(\mathbf{k}) \end{bmatrix}, \tag{4.13}$$

where f and g are 4×4 matrices, with the matrix elements

$$f_{\alpha\beta}(\mathbf{k})=(4/19\Gamma)\gamma_{\alpha\beta}{}^{+1-1}(\mathbf{k}), \tag{4.14}$$

$$g_{\alpha\beta}(\mathbf{k})=(4/19\Gamma)\gamma_{\alpha\beta}{}^{+1+1}(\mathbf{k}), \tag{4.15}$$

where $\alpha, \beta=1, 2, 3, 4$. Equations (4.9) and (4.10) are then written together in the form

$$(1/19\Gamma)[c_\mu(\mathbf{k}), H]=\sum_\nu[\delta_{\mu\nu}+F_{\mu\nu}(\mathbf{k})]c_\nu(\mathbf{k}). \tag{4.16}$$

In terms of the operators $c_\mu(\mathbf{k})$ the approximate commutation relations (4.2) and (4.3) are

$$[c_\mu(\mathbf{k}), c_\nu{}^\dagger(\mathbf{k}')]=\delta_{\mu\nu}\delta_{kk'}. \tag{4.17}$$

C. Elementary Excitations

The problem now is to find the proper creation and annihilation operators of the system. These operators are some linear combination of the operators $c_\mu(\mathbf{k})$, and they must satisfy on equation of motion of the form

$$[d_\mu(\mathbf{k}), H]=\epsilon_\mu(\mathbf{k})d_\mu(\mathbf{k}), \qquad \mu=1, 2\cdots 8 \tag{4.18}$$

where $\epsilon_\mu(\mathbf{k})$ is the (first-order) excitation energy for an elementary excitation labeled by a mode index μ and wave vector $\mathbf{k}$. The problem is thus reduced to solving the secular equation

$$\sum_\nu[(1-\omega_\mu(\mathbf{k}))\delta_{\mu\nu}+F_{\mu\nu}(\mathbf{k})]c_\nu(\mathbf{k})=0, \tag{4.19}$$

with $\omega_\mu(\mathbf{k})=\epsilon_\mu(\mathbf{k})/(19\Gamma)$. Equivalently, one writes

$$\sum_{\sigma\lambda}V_{\sigma\mu}{}^*(\mathbf{k})M_{\sigma\lambda}(\mathbf{k})V_{\lambda\mu}(\mathbf{k})=\omega_\mu(\mathbf{k})\delta_{\mu\nu}, \tag{4.20}$$

where

$$M_{\mu\nu}(\mathbf{k})=\delta_{\mu\nu}+F_{\mu\nu}(\mathbf{k}). \tag{4.21}$$

Here $V(\mathbf{k})$ is an orthogonal matrix with the properties

$$\sum_\lambda V_{\mu\lambda}{}^*V_{\nu\lambda}=\delta_{\mu\nu}, \qquad (V^{-1})_{\mu\nu}=V_{\nu\mu}{}^*. \tag{4.22}$$

The operators $d_\mu(\mathbf{k})$ are related to the $c_\mu(\mathbf{k})$'s by the

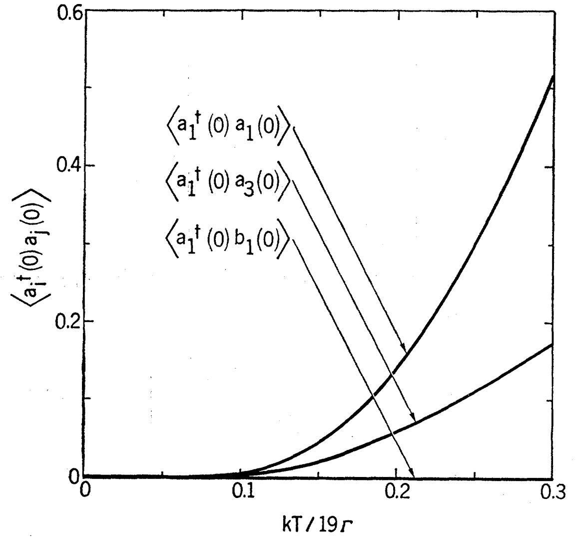

FIG. 2. The statistical averages $\langle a_1{}^\dagger(\mathbf{k})a_1(\mathbf{k})\rangle$, $\langle a_1{}^\dagger(\mathbf{k})a_3(\mathbf{k})\rangle$, and $\langle a_1{}^\dagger(\mathbf{k})b_1(\mathbf{k})\rangle$ for $\mathbf{k}=0$ as a function of temperature for the first-order linear spin-wave theory.

orthogonal transformation

$$d_\mu(\mathbf{k})=\sum_\nu V_{\nu\mu}{}^*(\mathbf{k})\,c_\nu(\mathbf{k}), \tag{4.23}$$

$$c_\mu(\mathbf{k})=\sum_\nu V_{\mu\nu}(\mathbf{k})\,d_\nu(\mathbf{k}). \tag{4.24}$$

The excitation energies $\epsilon_\mu(\mathbf{k})=19\Gamma\omega_\mu(\mathbf{k})$ are found by computing the eigenvalues $\omega_\mu(\mathbf{k})$ of the 8×8 matrix $M(\mathbf{k})$. For arbitrary values of $\mathbf{k}$ the eigenvalues and eigenvectors must be found numerically with the aid of a computer. The matrix elements $F_{\mu\nu}(\mathbf{k})$ are calculated using Eqs. (4.14), (4.15), (4.11), (2.6), and (2.9). A Table is given in Appendix B for values of m, $n=\pm 1$. Alternatively one may use the tabulations of Miyagi and Nakumura[9] in the manner described in Appendix A.

The excitation spectrum obtained here is somewhat different from that of Homma *et al.*[11] For example, at $\mathbf{k}=0$ the values of $\omega_\mu(\mathbf{k})$ are 1.450(3), 0.784(3), and 0.649(2), where the numbers in brackets indicate the degeneracy. Thus the excitation spectrum calculated here spreads over a somewhat larger energy range than the one predicted by Homma *et al.*

Thermodynamic averages involving the operators $d_\mu(\mathbf{k})$ are easily calculated using the basic equations (2.9a) and (2.9b) of the statistical perturbation method of Wallace.[12] These equations apply here exactly since the equivalent of Wallace's Eq. (2.1) is our Eq. (4.18). Following Wallace, one finds from Eq. (4.18) that

$$\langle d_\mu{}^\dagger(\mathbf{k}),\, d_\nu(\mathbf{k}')\rangle=\langle[d_\nu(\mathbf{k}'),\, d_\mu{}^\dagger(\mathbf{k})]\rangle\phi_\mu(\mathbf{k}). \tag{4.25}$$

where

$$\phi_\mu(\mathbf{k})=[\exp(\beta\epsilon_\mu(\mathbf{k}))-1]^{-1}, \tag{4.26}$$

$\beta=1/kT$, and the brackets $\langle\;\rangle$ indicate statistical averages.[12] Expanding the $d_\mu(\mathbf{k})$ operators in terms of the $c_\mu(\mathbf{k})$'s as in Eq. (4.23), and then using Eqs. (4.22) and the commutation relations (4.17) one finds

$$[d_\nu(\mathbf{k}'),\, d_\mu(\mathbf{k})]=\delta_{\mu\nu}\delta_{kk'}, \tag{4.27}$$

so that

$$\langle d_\mu{}^\dagger(\mathbf{k})\, d_\nu(\mathbf{k}')\rangle=\delta_{\mu\nu}\delta_{kk'}\phi_\mu(\mathbf{k}). \tag{4.28}$$

From Eqs. (4.22) and (4.23) it also follows that

$$\sum_\mu c_\mu{}^\dagger(\mathbf{k})\,c_\mu(\mathbf{k})=\sum_\nu d_\nu{}^\dagger(\mathbf{k})\,d_\nu(\mathbf{k}). \tag{4.29}$$

Since all sites are equivalent it is reasonable to assume here the molecular-field result

$$\langle J_i{}^z\rangle=\langle J^z\rangle=0,$$

or

$$\langle a_i{}^\dagger a_i\rangle=\langle a^\dagger a\rangle=\langle b^\dagger b\rangle,$$

independent of the lattice site i. Then

$$\begin{aligned}\langle a^\dagger a\rangle&=(4/N)\sum_{i(\alpha)}\langle a_{i(\alpha)}{}^\dagger a_{i(\alpha)}\rangle,\\&=(4/N)\sum_k\langle a_\alpha{}^\dagger(\mathbf{k})\,a_\alpha(\mathbf{k})\rangle,\\&=(1/N)\sum_{k\alpha}\langle a_\alpha{}^\dagger(\mathbf{k})\,a_\alpha(\mathbf{k})\rangle,\qquad \alpha=1,2,3,4\end{aligned} \tag{4.30}$$

where Eq. (4.30) follows from the transformation (4.7). In terms of the operators $c_\mu(\mathbf{k})$ one finds

$$\langle a^\dagger a\rangle=(1/2N)\sum_{k\mu}\langle c_\mu{}^\dagger(\mathbf{k})\,c_\mu(\mathbf{k})\rangle. \tag{4.31}$$

Then with the aid of Eqs. (4.28) and (4.29) we have

$$\langle a^\dagger a\rangle=(1/2N)\sum_{k\mu}\phi_\mu(\mathbf{k}), \tag{4.32}$$

where $\mu=1, 2\cdots 8$, and the sum on $\mathbf{k}$ extends over the first Brillouin zone.

Statistical averages like $\langle a^\dagger a\rangle$ can be estimated by replacing the sum in Eq. (4.32) by an integral:

$$(4/N)(1/8)\sum_{k\mu}\rightarrow\int g(\omega)\,d\omega, \tag{4.33}$$

where here the energy distribution function must satisfy the conditions

$$\int g(\omega)\,d\omega=1,\qquad \int \omega g(\omega)\,d\omega=1. \tag{4.34}$$

The second of these relations follows from the property

$$\mathrm{Tr}M(\mathbf{k})=\mathrm{Tr}\omega(\mathbf{k})=1, \tag{4.35}$$

where $\omega(\mathbf{k})$ is the matrix with the matrix elements $\omega_\mu(\mathbf{k})\delta_{\mu\nu}$. The energy state density $g(\omega)$ is determined by an energy-sampling method over values of $\mathbf{k}$ distributed through the Brillouin zone.[11,13]

The matrices $V(\mathbf{k})$ can also be calculated numerically. One can then use Eqs. (4.24) and (4.28) to find the thermodynamic averages $\langle c_\mu{}^\dagger(\mathbf{k})\,c_\nu(\mathbf{k})\rangle$, or by

Eqs. (4.7) and (4.8) the correlation functions $\langle c_{i(\mu)}{}^{\dagger} c_{\ (\nu)}\rangle$. As an example, plots of $\langle a_1{}^{\dagger}(\mathbf{k})a_1(\mathbf{k})\rangle$, $\langle a_1{}^{\dagger}(\mathbf{k})a_3(\mathbf{k})\rangle$, and $\langle a_1{}^{\dagger}(\mathbf{k})b_1(\mathbf{k})\rangle$ are shown in Fig. 2 for $\mathbf{k}=0$ as a function of temperature. The results of this approximation are of course only valid at very low temperatures.

V. NONLINEAR SPIN-WAVE APPROXIMATION

A. Equations of Motion

The problem now is to extend the formalism developed in Sec. IV to finite temperatures. Using the complete Hamiltonian (3.15) and the exact commutation relations (3.3) to (3.7) one finds

$$[a_i, H]=2\sum_j\Big\{\sum_{m=-2}^{+2}[3\gamma_{ij}{}^{0m}a_i+2\gamma_{ij}{}^{+2m}b_i]\Theta_j{}^m +\sqrt{2}\sum_{m=\pm1}[\gamma_{ij}{}^{+1m}(1-2n_{ai}-n_{bi})+\gamma_{ij}{}^{-1m}b_i{}^{\dagger}a_i]\Theta_j{}^m\Big\}, \tag{5.1}$$

and corresponding equations of motion for b_i, $a_i{}^{\dagger}$, and $b_i{}^{\dagger}$. In the molecular-field treatment one retains only the first term. Equation (5.1) illustrates the complexity of the problem at this point. To facilitate a solution of these equations of motion, one usually decouples these equations in some manner. In such a decoupling scheme certain groups of operators are replaced by their average values.[12]

The simplest approximation one can make at this point is the Tyablikov decoupling scheme, which was used in the molecular-field treatment of this problem, where a Green's-function formalism was used.[10] In terms of the operators used in this paper one decouples, for example,

$$\langle\langle a_i{}^{\dagger}a_ib_j;B_l\rangle\rangle \xrightarrow[i\neq j]{} \langle a_i{}^{\dagger}a_i\rangle\langle\langle b_j;B_l\rangle\rangle, \tag{5.2}$$

where the single brackets $\langle\ \rangle$ indicate statistical averages, and the double brackets $\langle\langle\ ;\ \rangle\rangle$ the Fourier transforms of the Green's functions.[10] Similar expressions are obtained for other combinations of operators. However, at this point, one retains only those terms where the averages $\langle\ \rangle$ on the right-hand side of Eq. (5.2) have diagonal matrix elements when operating on the states $|n_{ai}, n_{bi}\rangle$. Since we are ultimately only interested in statistical averages, this decoupling approximation can equally well be applied to an equation-of-motion technique, where the equivalent of Eq. (5.2) is

$$a_i{}^{\dagger}a_ib_j \xrightarrow[i\neq j]{} \langle a_i{}^{\dagger}a_i\rangle b_j, \qquad \text{(Tyablikov decoupling)}, \tag{5.3}$$

and similar expressions for other combinations of operators satisfying the condition that the operators in the brackets $\langle\ \rangle$ be diagonal for the states $|n_{ai}, n_{bi}\rangle$. The fact that this decoupling scheme is not a particularly good one for this problem can, for example, be seen from the linear spin-wave results as given in Fig. 2, which shows that terms like $\langle a_i{}^{\dagger}b_j\rangle$ $(i\neq j)$ could become appreciable. The effect of a higher-order decoupling approximation must therefore be considered ultimately. The decoupling scheme used by Ueyama and Matsubara[13] seems to be equivalent to Eq. (5.3).

An application of the decoupling approximations (5.2) and (5.3) then yields the much simpler equations of motion

$$(-\tfrac{1}{2}\langle\Theta^0\rangle)^{-1}[a_i, H]=19\Gamma a_i +4\sum_j[\gamma_{ij}{}^{+1-1}(a_j-b_j{}^{\dagger})-\gamma_{ij}{}^{+1+1}(b_j-a_j{}^{\dagger})], \tag{5.4}$$

where we have used the equation $\gamma_{ij}{}^{00}=-(19/144)\Gamma$, the nearest-neighbor restriction (2.13), and the equivalence of sites, together with the molecular-field result $\langle J^z\rangle=0$, as in Sec. IV, $\langle a_i{}^{\dagger}a_i\rangle=\langle a^{\dagger}a\rangle=\langle b^{\dagger}b\rangle$, so that, by Eq. (3.12),

$$\langle a^{\dagger}a\rangle=\langle b^{\dagger}b\rangle=\tfrac{1}{3}+\tfrac{1}{6}\langle\Theta^0\rangle. \tag{5.5}$$

It is seen that except for the factor $(-\frac{1}{2}\langle\Theta^0\rangle)^{-1}$ and the $a_j{}^{\dagger}$ and $b_j{}^{\dagger}$ terms, Eq. (5.4) is identical to Eq. (4.5) of the first-order linear spin-wave approximation. Thus again, as in Sec. IV, only the terms involving $\gamma_{ij}{}^{mn}$, with m, $n=0$, ±1, are retained in the equations of motion (5.1) to yield Eq. (5.4). Therefore one may replace the complete Hamiltonian (2.8) by an effective Hamiltonian valid only within the decoupling approximation (5.3)

$$H_{\text{eff}}=H^0+H', \tag{5.6}$$

where

$$H^0=\sum_{ij}\gamma_{ij}{}^{00}\Theta_i{}^0\Theta_j{}^0 \tag{5.7}$$

is the molecular-field Hamiltonian,[10] and

$$H'=\sum_{ij}\sum_{mn}\gamma_{ij}{}^{mn}\Theta_i{}^m\Theta_j{}^n, \qquad m, n=\pm1. \tag{5.8}$$

As in Sec. IV, Eq. (5.4) can be Fourier-analyzed with the result

$$\begin{aligned}(-\tfrac{1}{2}\langle\Theta^0\rangle 19\Gamma)^{-1}[a_\alpha(\mathbf{k}), H] &=a_\alpha(\mathbf{k})+\sum_\beta f_{\alpha\beta}(\mathbf{k})[a_\beta(\mathbf{k})-b_\beta{}^{\dagger}(-\mathbf{k})]\\ &\quad-\sum_\beta g_{\alpha\beta}(\mathbf{k})[b_\beta(\mathbf{k})-a_\beta{}^{\dagger}(-\mathbf{k})],\end{aligned} \tag{5.9}$$

where $a_\alpha(\mathbf{k})$ and $b_\alpha(\mathbf{k})$ are given by Eqs. (4.7) and (4.8), and $f_{\alpha\beta}(\mathbf{k})$ and $g_{\alpha\beta}(\mathbf{k})$ by Eqs. (4.14) and (4.15), respectively. The corresponding equation for $b_\alpha(\mathbf{k})$ is

$$\begin{aligned}(-\tfrac{1}{2}\langle\Theta^0\rangle 19\Gamma)^{-1}[b_\alpha(\mathbf{k}), H] &=b_\alpha(\mathbf{k})-\sum_\beta g_{\alpha\beta}{}^*(\mathbf{k})[a_\beta(\mathbf{k})-b_\beta{}^{\dagger}(-\mathbf{k})],\\ &\quad+\sum_\beta f_{\alpha\beta}{}^*(\mathbf{k})[b_\beta(\mathbf{k})-a_\beta{}^{\dagger}(-\mathbf{k})].\end{aligned} \tag{5.10}$$

The equations of motion for $a_\alpha{}^{\dagger}(-\mathbf{k})$ and $b_\alpha{}^{\dagger}(-\mathbf{k})$ are found by taking the Hermitian conjugates of Eqs. (5.9) and (5.10). In terms of the operators $c_\mu(\mathbf{k})$, defined by Eq. (4.12), Eqs. (5.9) and (5.10) are

$$(-\tfrac{1}{2}\langle\Theta^0\rangle 19\Gamma)^{-1}[c_\mu, H]=c_\mu+\sum_\nu(F_{\mu\nu}c_\nu+F_{\mu\nu}'c_\nu^\dagger), \tag{5.11}$$

where the matrix F is defined by Eq. (4.13) and F' is the 8×8 matrix

$$F'=\begin{bmatrix} g & -f \\ -f^* & g^* \end{bmatrix}. \tag{5.12}$$

Here and below, for the sake of simplicity, the indices $\mathbf{k}$ have been left off. Following Sec. IV, the problem now is to solve the equations of motion (5.9) and (5.10), or equivalently (5.11), in order to obtain the elementary excitation operators and energies for the system. This method seems at first sight to involve the diagonalization of a 16×16 matrix, since the sixteen operators $a_1(\mathbf{k})$, $a_2(\mathbf{k})\cdots b_4^\dagger(-\mathbf{k})$ are coupled by the equations of motion (5.9) and (5.10). This problem can however be reduced to an 8×8 diagonalization in a manner indicated below.

Taking the commutator of Eqs. (5.9) and (5.10) with the Hamiltonian one finds

$$(-\tfrac{1}{2}\langle\Theta^0\rangle 19\Gamma)^{-2}[[a_\alpha, H], H]=a_\alpha+2\sum_\beta(f_{\alpha\beta}a_\beta-g_{\alpha\beta}b_\beta), \tag{5.13}$$

$$(-\tfrac{1}{2}\langle\Theta^0\rangle 19\Gamma)^{-2}[[b_\alpha, H], H] =b_\alpha+2\sum_\beta(-g_{\alpha\beta}^*a_\beta+f_{\alpha\beta}^*b_\beta), \tag{5.14}$$

where $\alpha=1, 2, 3, 4$. Equivalently, in terms of the operators c_μ

$$(-\tfrac{1}{2}\langle\Theta^0\rangle 19\Gamma)^{-2}[[c_\mu, H], H]=\sum_\nu(\delta_{\mu\nu}+2F_{\mu\nu})c_\nu, \tag{5.15}$$

where $\mu, \nu=1, 2\cdots8$.

B. Elementary Excitations

As in Sec. IV, the elementary excitation operators must obey equations of motion of the form

$$[f_\mu, H]=\epsilon_\mu f_\mu, \tag{5.16}$$

$$[f_\mu^\dagger, H]=-\epsilon_\mu f_\mu^\dagger, \tag{5.17}$$

where $\epsilon_\mu(\mathbf{k})$ are the elementary excitation energies of the system and $\mu=1, 2\cdots8$. Combining Eqs. (5.16) and (5.17) one finds

$$[[d_\mu, H], H]=\epsilon_\mu^2 d_\mu, \tag{5.18}$$

where here d_μ is a linear combination of the operators f_μ and $f_\mu^\dagger$:

$$d_\mu=\alpha_\mu f_\mu+\beta_\mu f_\mu^\dagger. \tag{5.19}$$

Following the arguments of Sec. IV one finds from Eqs. (5.15) and (5.19) that the operators $d_\mu(\mathbf{k})$ are related to the $c_\mu(\mathbf{k})$'s by

$$d_\mu=\sum_\nu V_{\nu\mu}^*c_\nu, \tag{5.20}$$

$$c_\mu=\sum_\nu V_{\mu\nu}d_\nu, \tag{5.21}$$

where $\mu, \nu=1, 2\cdots8$. Here the orthogonal transformation that diagonalizes the matrix $M(\mathbf{k})$ is

$$\sum_{\sigma\lambda}V_{\mu\sigma}^*M_{\mu\nu}V_{\nu\lambda}=\omega_\mu^2\delta_{\mu\nu}, \qquad \mu, \nu, \sigma, \lambda=1, 2\cdots8, \tag{5.22}$$

where

$$\omega_\mu(\mathbf{k})=(\tfrac{1}{2}\langle\Theta^0\rangle 19\Gamma)^{-1}\epsilon_\mu(\mathbf{k}), \tag{5.23}$$

and

$$M_{\mu\nu}(\mathbf{k})=\delta_{\mu\nu}+2F_{\mu\nu}(\mathbf{k}). \tag{5.24}$$

Here the matrices M and V are of course different from those defined in Sec. IV, however they do satisfy the same orthonormality condition (4.22). Using Eq. (4.22) one may invert Eq. (5.22) to obtain

$$M_{\mu\nu}=\sum_\lambda V_{\mu\lambda}V_{\nu\lambda}^*\omega_\lambda^2. \tag{5.25}$$

The equations of motion for the operators $d_\mu(\mathbf{k})$ do not have the same form as Eq. (4.18), since the $d_\mu(\mathbf{k})$'s are not the elementary excitation operators when one goes beyond a first-order perturbation treatment. Instead one finds, from Eqs. (5.16), (5.17), and (5.19),

$$(-\tfrac{1}{2}\langle\Theta^0\rangle 19\Gamma)^{-1}[d_\mu, H]=\xi_\mu d_\mu+\eta_\mu d_\mu^\dagger, \tag{5.26}$$

where Eq. (5.18) is satisfied by

$$\xi_\mu^2-\eta_\mu^2=\omega_\mu^2. \tag{5.27}$$

Equations (5.16), (5.17), and (5.26) are jointly satisfied for the choices

$$\alpha_\mu=\tfrac{1}{2}[1+(\xi_\mu/\omega_\mu)], \qquad \beta_\mu=-\eta_\mu/(2\omega_\mu), \tag{5.28}$$

so that, from Eq. (5.19),

$$d_\mu=(\eta_\mu/2\omega_\mu)\{[(\xi_\mu+\omega_\mu)/\eta_\mu]f_\mu-f_\mu^\dagger\}. \tag{5.29}$$

Here $\omega_\mu(\mathbf{k})$ is specified by Eq. (5.22), and $\xi_\mu(\mathbf{k})$ and $\eta_\mu(\mathbf{k})$ have yet to be determined. $d_\mu^\dagger(\mathbf{k})$ is found by taking the Hermitian conjugate of Eq. (5.29). The inverse transformations are

$$f_\mu=d_\mu+[(\xi_\mu-\omega_\mu)/\eta_\mu]d_\mu^\dagger, \tag{5.30}$$

and its Hermitian conjugate.

The quantities $\xi_\mu(\mathbf{k})$ and $\eta_\mu(\mathbf{k})$ are evaluated as follows. By Eq. (5.20) one has

$$[d_\mu, H]=\sum_\nu V_{\nu\mu}^*[c_\nu, H]. \tag{5.31}$$

An application of Eq. (5.11) yields

$$(-\tfrac{1}{2}\langle\Theta^0\rangle 19\Gamma)^{-1}[d_\mu, H] =\sum_{\nu\lambda}[(\delta_{\nu\lambda}+F_{\nu\lambda})V_{\nu\mu}^*c_\lambda+F_{\nu\lambda}'V_{\nu\lambda}^*c_\lambda^\dagger]. \tag{5.32}$$

Also

$$\xi_\mu d_\mu + \eta_\mu d_\mu{}^\dagger = \sum_\nu (\xi_\mu V_{\nu\mu}{}^* c_\nu + \eta_\mu V_{\nu\mu} c_\nu{}^\dagger). \quad (5.33)$$

Substituting Eqs. (5.32) and (5.33) into Eq. (5.26), and equating coefficients of c_λ and $c_\lambda{}^\dagger$, or alternatively d_μ and $d_\mu{}^\dagger$, one finds, with the help of Eqs. (5.25), (5.24), and the orthonormality condition (4.22), that

$$\xi_\mu(k) = \tfrac{1}{2}[1+\omega_\mu(\mathbf{k})^2], \quad (5.34)$$

$$F_{\mu\nu}{}' V_{\mu\lambda}{}^* = \eta_\nu V_{\nu\lambda} \delta_{\nu\mu}. \quad (5.35)$$

C. Excitation Spectrum

The elementary excitation energies $\epsilon_\mu(\mathbf{k})$ can again be calculated numerically from Eqs. (5.22), (5.23), and (5.24) by diagonalizing the matrix $M(\mathbf{k})$. The eigenvalues obtained agree well with those found by Ueyama and Matsubara.[13] For example at $\mathbf{k}=0$, the values obtained for $\omega_\mu(\mathbf{k})$ are 1.378(3), 0.754(3), and 0.546(2), where the numbers in brackets indicate the degeneracy. One should note that these results are close to the first-order perturbation values obtained in Sec. IV. Thus at $\mathbf{k}=0$ and $T=0$ the energy gap is $\Delta\epsilon(0)=10.4\Gamma$. For a value of $eQ=0.1348\times10^{-16}$ electron cm^2 (free-H$_2$ molecular quadrupole moment), or $\Gamma=0.982$°K^2, one finds $\Delta\epsilon(0)=10.2$°K. A discussion of the possibility of an experimental observation of this energy gap is given in Sec. VIII. As an example of the energy spectrum, Fig. 3 shows $\omega_\mu(\mathbf{k})$ as a function of $\mathbf{k}$ for the [100] direction. It follows from Eq. (5.23) that the energy levels $\epsilon_\mu(\mathbf{k})$ have the same temperature dependence as $\langle \mathcal{O}^0 \rangle$, as discussed in Sec. VI.

VI. CALCULATION OF $\langle (J^z)^2 \rangle$

A. Statistical Averages

The calculation of statistical averages follows in the same manner as in Sec. IV. It follows from Eq. (5.21) that

$$\langle c_\mu{}^\dagger c_\nu \rangle = \sum_{\lambda\sigma} V_{\mu\lambda}{}^* V_{\nu\sigma} \langle d_\lambda{}^\dagger d_\sigma \rangle. \quad (6.1)$$

Using Eq. (5.29) one finds

$$\langle d_\lambda{}^\dagger d_\sigma \rangle = [\eta_\lambda \eta_\sigma / (4\omega_\lambda \omega_\sigma)] \times \langle \{ f_\lambda - [(\xi_\lambda+\omega_\lambda)/\eta_\lambda] f_\lambda{}^\dagger \} \{ f_\sigma{}^\dagger - [(\xi_\sigma+\omega_\sigma)/\eta_\sigma] f_\sigma \} \rangle \quad (6.2)$$

Again applying Wallace's result, one obtains from Eqs. (5.16) and (5.17)

$$\langle f_\lambda{}^\dagger f_\sigma \rangle = \langle [f_\sigma, f_\lambda{}^\dagger] \rangle \phi_\lambda, \quad (6.3)$$

where

$$\phi_\lambda(\mathbf{k}) = [\exp(\beta\epsilon_\lambda(\mathbf{k}))-1]^{-1}. \quad (6.4)$$

The statistical average of the commutator in Eq. (6.3) is found from the relation

$$\langle [c_\mu, c_\nu{}^\dagger] \rangle = -\tfrac{1}{2} \langle \mathcal{O}^0 \rangle \delta_{\mu\nu}, \quad (6.5)$$

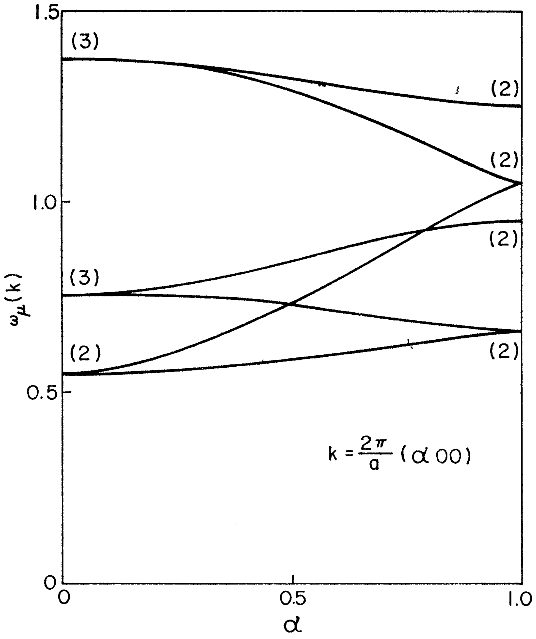

FIG. 3. Excitation spectrum for the [100] direction. The numbers in brackets indicate the degeneracy.

which is valid within the decoupling approximation described in Sec. V. It then follows from Eqs. (4.22) and (5.20) that

$$\langle [d_\mu, d_\nu{}^\dagger] \rangle = -\tfrac{1}{2} \langle \mathcal{O}^0 \rangle \delta_{\mu\nu}, \quad (6.6)$$

so that, by Eq. (5.30),

$$\langle [f_\mu, f_\nu{}^\dagger] \rangle = -\tfrac{1}{2} \langle \mathcal{O}^0 \rangle \{1-[(\xi_\mu-\omega_\mu)/\eta_\mu]^{-2}\} \delta_{\mu\nu}, \quad (6.7)$$

$$\langle [f_\mu, f_\nu] \rangle = 0. \quad (6.8)$$

An application of Eq. (6.3), (6.7), and (6.8) yields for Eq. (6.2)

$$\langle d_\lambda{}^\dagger d_\sigma \rangle = -\tfrac{1}{2} \langle \mathcal{O}^0 \rangle [\eta_\lambda{}^2/(4\omega_\lambda{}^2)] \{1-[(\xi_\lambda-\omega_\lambda)^2/\eta_\lambda{}^2]\} \times \{1+[1+(\xi_\lambda+\omega_\lambda)^2/\eta_\lambda{}^2]\phi_\lambda\} \delta_{\lambda\sigma}. \quad (6.9)$$

Using Eq. (5.27), one reduces Eq. (6.9) to

$$\langle d_\lambda{}^\dagger d_\sigma \rangle = \tfrac{1}{4} \langle \mathcal{O}^0 \rangle [1-(\xi_\lambda/\omega_\lambda) \coth(\beta\epsilon_\lambda/2)] \delta_{\lambda\sigma}, \quad (6.10)$$

so that, by Eq. (5.34), one finds for Eq. (6.1)

$$\langle c_\mu{}^\dagger c_\nu \rangle = \tfrac{1}{4} \langle \mathcal{O}^0 \rangle \sum_\lambda V_{\mu\nu}{}^* V_{\nu\lambda} \{1-\tfrac{1}{2}[(1+\omega_\lambda{}^2)/\omega_\lambda] \coth(\beta\epsilon_\lambda/2)\}. \quad (6.11)$$

As in Sec. IV it is seen then that

$$\langle a^\dagger a \rangle = \tfrac{1}{4} \langle \mathcal{O}^0 \rangle \{1-(1/4N) \sum_{k\mu} [(1+\omega_\mu{}^2)/\omega_\mu] \coth(\beta\epsilon_\mu/2)\}. \quad (6.12)$$

Eq. (6.12) can be rewritten in terms of $\langle\mathcal{O}^0\rangle$ entirely:

$$\langle\mathcal{O}^0\rangle=4+(3\langle\mathcal{O}^0\rangle/4N)\sum_{k\mu}[(1+\omega_\mu^2)/\omega_\mu]\coth(\beta\epsilon_\mu/2), \tag{6.13}$$

where ϵ_μ is specified by Eq. (5.23):

$$\epsilon_\mu(k)=-\tfrac{1}{2}\langle\mathcal{O}^0\rangle 19\Gamma\omega_\mu(k). \tag{6.14}$$

$\langle(J^z)^2\rangle$ is found from Eq. (2.7):

$$\langle(J^z)^2\rangle=\tfrac{1}{3}(\langle\mathcal{O}^0\rangle+2). \tag{6.15}$$

By simply setting $\omega_\mu(\mathbf{k})=1$ in Eq. (6.13) one obtains the molecular-field result of Ref. 10. One should note that Eq. (6.13) differs somewhat from the equivalent result of Ueyama and Matsubara,[13] and thus leads to the different results obtained below.

As in Sec. IV, Eq. (6.13) can be solved for $\langle\mathcal{O}^0\rangle$, or $\langle(J^z)^2\rangle$, by replacing the sum of μ and $\mathbf{k}$ by an integral, defined as in Eq. (4.33), where now, however, the energy density $g(\omega)$ must satisfy the conditions

$$\int g(\omega)d\omega=1, \qquad \int \omega^2 g(\omega)d\omega=1. \tag{6.16}$$

The second of these relations, again, as in Eq. (4.35) follows from the invariance property of the trace. Again $g(\omega)$ can be determined numerically in the manner described by Homma *et al.*,[11] and Ueyama and Matsubara.[13] Evaluating these sums one finds small but nonzero deviations from the molecular-field results at all temperatures. These deviations are calculated below for both zero temperature and the branching temperature.

B. Zero-Temperature Results

At $T=0$, Eq. (6.13) reduces to

$$\langle\mathcal{O}^0\rangle_0=4+(3\langle\mathcal{O}^0\rangle_0/4N)\sum_{k\mu}[(1+\omega_\mu^2)/\omega_\mu], \tag{6.17}$$

$$=4+(3\langle\mathcal{O}^0\rangle_0/2)(I_{+1}+I_{-1}), \tag{6.18}$$

where

$$I_n\equiv(1/2N)\sum_{k\mu}[\omega_\mu(k)]^n\rightarrow\int\omega^n g(\omega)d\omega, \tag{6.19}$$

with n a positive or negative integer. Here the subscript 0 indicates evaluation at $T=0$. Equation (6.18) is solved for $\langle\mathcal{O}^0\rangle_0$:

$$\langle\mathcal{O}^0\rangle_0=-8[3(I_{+1}+I_{-1})-2]^{-1}. \tag{6.20}$$

From the approximate energy density of Ueyama and Matsubara[13] one finds $I_{+1}=0.994$ and $I_{-1}=1.035$, so that $\langle\mathcal{O}^0\rangle_0\cong-1.957$. Since the molecular-field result is -2, one has

$$\langle\mathcal{O}^0\rangle_0-(\langle\mathcal{O}^0\rangle_0)_{\text{MFA}}\cong+0.04, \tag{6.21}$$

or about a 2% deviation from the molecular-field result. This deviation is due to the spin-wave zero-point motion.

C. Branching Temperature

An indication of the effect of the spin-wave excitations at higher temperatures is given by a determination of how the branching temperature for Eq. (6.13) compares with the corresponding value for the molecular-field approximation. The branching temperature is defined as that temperature at which a nonzero solution to Eq. (6.13) first occurs. For second-order transitions the branching temperature corresponds to the critical temperature. For first-order transitions, as is the case for solid ortho-H_2, the solution to Eq. (6.13) very close to the branching temperature is not a stable solution.[2,10]

For large temperatures the coth in Eq. (6.13) can be expanded:

$$\coth(\beta\epsilon_\mu/2)=2/(\beta\epsilon_\mu)+\beta\epsilon_\mu/6-\cdots, \tag{6.22}$$

so that

$$\langle\mathcal{O}^0\rangle=4-6(kT/19\Gamma)(1+I_{-2})+O(\langle\mathcal{O}^0\rangle), \tag{6.23}$$

where I_{-2} is specified by Eq. (6.19) with $n=-2$. Again using the approximate energy density of Ueyama and Matsubara[13] one finds $I_{-2}=1.102$. One defines $T=T_b$ when $\langle\mathcal{O}^0\rangle=0$, thus Eq. (6.23) gives $kT_b\cong0.95(19\Gamma/3)$, or a deviation of about 5% from the molecular-field value $19\Gamma/3$. The actual transition temperature T_c between the ordered and disordered phases can be expected to deviate by about the same amount.[2]

Except for these small deviations, the qualitative behavior of $\langle(J^z)^2\rangle$ versus T is the same as calculated for the molecular-field approximation.[2,10] It is thus seen that because of the large energy gap in the excitation spectrum, using a Tyablikov decoupling scheme as outlined in Sec. V, the $\mathbf{k}$-dependent spin-wave excitations have only a very small effect on the thermodynamic properties of the system, both at low and high temperatures. Further discussion is given in Sec. VIII.

VII. ZERO-POINT ENERGY

The zero-point energy due to the spin-wave excitations can be calculated by evaluating the statistical average of the Hamiltonian effective in this decoupling approximation. This effective Hamiltonian is given by Eqs. (5.6), (5.7), and (5.8). Decoupling in the usual manner one obtains

$$\langle H^0\rangle=-19\Gamma N(\tfrac{1}{3}-2\langle a^\dagger a\rangle+3\langle a^\dagger a\rangle^2). \tag{7.1}$$

The statistical average of H' is most easily found in the following fashion. Using the transformations (4.7) and (4.8), H' is written

$$H'=2\sum_{\alpha\beta k}[\gamma_{\alpha\beta}^{+1-1}(a_\alpha^\dagger a_\beta+b_\alpha b_\beta^\dagger-a_\alpha^\dagger b_\beta^\dagger-b_\alpha a_\beta) -\gamma_{\alpha\beta}^{+1+1}(a_\alpha^\dagger b_\beta+b_\alpha a_\beta^\dagger-a_\alpha^\dagger a_\beta^\dagger-b_\alpha b_\beta)+\text{H.c.}] \tag{7.2}$$

where, as before, H.c. indicates the Hermitian conjugate, and the variables $\mathbf{k}$, as in $a_\alpha(\mathbf{k})$, have been left off. In terms of the operators $c_\mu(\mathbf{k})$, given by Eq. (4.12), and the matrices $F(\mathbf{k})$ and $F'(\mathbf{k})$, given by

Eqs. (4.13) and (5.12), respectively, the statistical average $\langle H'\rangle$ is then

$$\langle H'\rangle=(19\Gamma/2)\sum_{\mu\nu k}(F_{\mu\nu}\langle c_\mu{}^\dagger c_\nu\rangle+F_{\mu\nu}'\langle c_\mu{}^\dagger c_\nu{}^\dagger\rangle+\text{H.c.}). \tag{7.3}$$

It follows from Eq. (6.1) that

$$\sum_{\mu\nu}F_{\mu\nu}\langle c_\mu{}^\dagger c_\nu\rangle=\sum_{\mu\nu\lambda}F_{\mu\nu}V_{\mu\lambda}{}^*V_{\nu\lambda}\langle d_\lambda{}^\dagger d_\lambda\rangle. \tag{7.4}$$

Again replacing $F_{\mu\nu}$ by $\frac{1}{2}(M_{\mu\nu}-\delta_{\mu\nu})$, as by Eq. (5.24), and using Eqs. (5.25) and (5.34), one finds

$$\sum_{\mu\nu}F_{\mu\nu}\langle c_\mu{}^\dagger c_\nu\rangle$$
$$=(1/16)\langle\Theta^0\rangle\sum_\lambda(1-\omega_\lambda{}^2)(1+\omega_\lambda{}^2)\omega_\lambda{}^{-1}\coth(\beta\epsilon_\lambda/2). \tag{7.5}$$

The other term in $\langle H'\rangle$ is

$$\sum_{\mu\nu}F_{\mu\nu}'\langle c_\mu{}^\dagger c_\nu{}^\dagger\rangle=\sum_{\mu\nu\lambda}F_{\mu\nu}'V_{\mu\lambda}{}^*V_{\mu\lambda}{}^*\langle d_\lambda{}^\dagger d_\lambda{}^\dagger\rangle, \tag{7.6}$$

$$=\sum_\lambda\eta_\lambda\langle d_\lambda{}^\dagger d_\lambda{}^\dagger\rangle. \tag{7.7}$$

The second step follows from Eqs. (4.22) and (5.35). One must now evaluate $\langle d_\lambda{}^\dagger d_\lambda{}^\dagger\rangle$. This is done in a manner similar to the calculation of $\langle d_\mu{}^\dagger d_\mu\rangle$ in Sec. VI. Using the Hermitian conjugate of Eq. (5.29), one finds

$$\langle d_\mu{}^\dagger d_\mu{}^\dagger\rangle=-(\eta_\mu{}^2/4\omega_\mu{}^2)[(\xi_\mu+\omega_\mu)/\eta_\mu]\langle[f_\mu,f_\mu{}^\dagger]\rangle(1+2\phi_\mu). \tag{7.8}$$

From Eqs. (4.22), (5.27), and (6.7), it then follows that

$$\langle d_\mu{}^\dagger d_\mu{}^\dagger\rangle=\tfrac{1}{4}\langle\Theta^0\rangle[(\xi_\mu{}^2-\omega_\mu{}^2)/(\omega_\mu\eta_\mu)](1+2\phi_\mu), \tag{7.9}$$

so that

$$\sum_{\mu\nu}F_{\mu\nu}'\langle c_\mu{}^\dagger c_\nu{}^\dagger\rangle$$
$$=(1/16)\langle\Theta^0\rangle\sum_\lambda(1-\omega_\lambda{}^2)^2\omega_\lambda{}^{-1}\coth(\beta\epsilon_\lambda/2). \tag{7.10}$$

Combining Eqs. (7.5) and (7.10) one has

$$\langle H'\rangle$$
$$=(19\Gamma/8)\langle\Theta^0\rangle\sum_{\mu k}[(1-\omega_\mu(\mathbf{k})^2)/\omega_\mu(\mathbf{k})]\coth(\beta\epsilon_\mu(\mathbf{k})/2), \tag{7.11}$$

where again

$$\epsilon_\mu(\mathbf{k})=-\tfrac{1}{2}\langle\Theta^0\rangle19\Gamma\omega_\mu(\mathbf{k}). \tag{7.12}$$

Equation (7.11) is the same as the equivalent result of Ueyama and Matsubara.[13] $\langle H\rangle=\langle H^0\rangle+\langle H'\rangle$ can again be estimated by evaluating the sum in Eq. (7.11) in the manner discussed in Secs. VI and VII. For example, at $T=0$, $\langle H^0\rangle+\langle H'\rangle$ is given by

$$\langle H^0\rangle_0+\langle H'\rangle_0=-19\Gamma N\{\tfrac{1}{3}-\tfrac{1}{2}\langle\Theta^0\rangle(1-I_{+1})$$
$$+(3/16)\langle\Theta^0\rangle^2[1-\tfrac{1}{2}(I_{+1}+I_{-1})]^2\}. \tag{7.13}$$

Using the values of I_{+1} and I_{-1} given in Sec. VII one finds

$$\langle H^0\rangle_0+\langle H'\rangle_0\cong-1.015(19\Gamma N/3), \tag{7.14}$$

or a decrease of the ground-state energy due to spin-wave zero-point motion of about 2% of the molecular-field value $19\Gamma N/3$.

VIII. CONCLUSIONS

An equation-of-motion treatment of the spin-wave approximation for fcc solid ortho-H_2, using a degenerate perturbation treatment based on the statistical perturbation theory of Wallace,[12] has been used to calculate the excitation spectrum, long-range order, and ground-state energy of fcc solid ortho-H_2. When the appropriate limits are taken, the results obtained here reduce to those of the molecular-field theory, derived previously.[1,2,10] There is some disagreement with the linear spin-wave results of Homma *et al.*,[11] and the Green's-function treatment Ueyama and Matsubara,[13] as discussed in detail above.

In particular, it is found that an energy gap of several degrees exists. The excitation energies should in principle be observable by either neutron diffraction, as suggested by Ueyama and Matsubara,[13] or by infrared and Raman spectra of solid ortho-hydrogen, in a manner similar to that of solid para-hydrogen.[16] It is also seen that the thermodynamic averages $\langle(J^z)^2\rangle$ and $\langle H\rangle$ differ only slightly from their molecular-field values, the zero-temperature values deviating by about 2%, and the transition temperature by approximately 5%. The latter change is in the right direction but not nearly big enough to bring agreement between the theoretical and experimental values of the transition temperature. Using a value of $eQ=0.1348\times10^{-16}$ electron cm^2, as in Sec. VI, the present theory gives $T_c\cong6.40$°K, with only nearest-neighbor interactions, compared to an extrapolated experimental value of about 2.8°K for pure ortho-H_2. However, four important facts have to be kept in mind. First, in this and previous papers,[2,10,17] only the fcc lattice was considered, while the actual transition is one which also involves a change in the molecular lattice from fcc to hcp.[17] Second, in all calculations we have used for Q the value for the quadrupole moment of a free-H_2 molecule. The effective quadrupole moment could well be smaller when the molecule is bound in the solid. Third, one should note that a replacement of the Tyablikov decoupling scheme used here by a higher-order approximation could lead to an improvement in the value of the transition temperature. Finally, the effect of lattice vibrations must be considered in a complete theory.[17]

Thus, experimental observations of the energy gap and the excitation energies would yield additional important information as to the correct value of Γ, or

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the value of the molecular quadrupole moment Q, in addition to a measurement of the transition temperature.

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APPENDIX A: RELATIONSHIP TO NAKAMURA'S HAMILTONIAN

The Hamiltonian used by Nakamura and others[3,9,13] has the form, in the notation of Nakamura,[9]

$$H=\tfrac{1}{2}\sum_{ij}\sum_{\mu\nu}Z_{\mu}{}^{i}\mathfrak{F}_{\mu\nu}(\mathbf{R}_i-\mathbf{R}_j)Z_{\nu}{}^{j},\qquad \mu,\nu=1,2\cdots5,\tag{A1}$$

where, for the coordinate systems used in this paper, $\mathfrak{F}_{\mu\nu}(\mathbf{R}_i-\mathbf{R}_j)$ is given by Nakamura's[9] Eqs. (4.4) and Tables II and VII. $Z_{\mu}{}^{i}$ is the μth quadrupole component of the ith molecule and is specified by Nakamura's[9] Table I. Equations (A1) and (2.8) are of course the same. We can thus find the relationship between $\mathcal{O}_j{}^m$ and $Z_{\mu}{}^{j}$, and the matrices γ and $\mathfrak{F}$. Using the operator equivalent equation[13] (for states with $J=1$)

$$Y_{2M}(j)\rightarrow\sum_{\mu}\mathfrak{D}_{M\mu}Z_{\mu}{}^{j},\tag{A2}$$

where $\mathfrak{D}_{M\mu}$, $M=-2,\cdots,+2$, $\mu=1,2\cdots5$, is the 5×5 matrix[13]

$$\mathfrak{D}=-[(3/10)]^{1/2}\begin{bmatrix}1/\sqrt{2} & 0 & 0 & 0 & -i/\sqrt{2}\\ 0 & 0 & i/\sqrt{2} & -1/\sqrt{2} & 0\\ 0 & 1 & 0 & 0 & 0\\ 0 & 0 & -i/\sqrt{2} & -1/\sqrt{2} & 0\\ 1/\sqrt{2} & 0 & 0 & 0 & i/\sqrt{2}\end{bmatrix},\tag{A3}$$

a comparison of Eqs. (2.5) and (A2), and Eqs. (2.8) and (A1) yields then

$$\mathcal{O}_j{}^m=(A_m)^{-1}\sum_{\mu}\mathfrak{D}_{M\mu}Z_{\mu}{}^{j},\tag{A4}$$

$$Z_{\mu}{}^{j}=\sum_{m}A_m(\mathfrak{D}^{-1})_{\mu m}\mathcal{O}^{\,m},\tag{A5}$$

$$\gamma_{ij}{}^{mn}=A_mA_n\sum_{\mu\nu}(\mathfrak{D}^{-1})_{\mu m}(\mathfrak{D}^{-1})_{\nu n}\mathfrak{F}_{\mu\nu}(\mathbf{R}_i-\mathbf{R}_j).\tag{A6}$$

APPENDIX B: TABULATION OF $F(\mathbf{k})$

The 8×8 matrix $F(\mathbf{k})$, given by Eqs. (4.13), (4.14), and (4.15), is specified in terms of the 4×4 matrices $f(\mathbf{k})$ and $g(\mathbf{k})$. A numerical evaluation of Eq. (2.9) yields

$$f=\begin{bmatrix}0 & x & y & z\\ x^* & 0 & z^* & y\\ y^* & z & 0 & x\\ z^* & y^* & x^* & 0\end{bmatrix},\qquad g=\begin{bmatrix}0 & u & v & w\\ u & 0 & w^* & v^*\\ v & w^* & 0 & u\\ w & v^* & u & 0\end{bmatrix}$$

where, for nearest neighbors only,

$$x=+0.08185(C_1+C_2)+0.01519i(C_1+C_2),$$
$$y=-0.05849(C_3+C_4)+0.02534i(C_3-C_4),$$
$$z=-0.02779(C_5+C_6)-0.07852i(C_5+C_6),$$
$$u=-0.05849(C_1+C_2)-0.02534i(C_1-C_2),$$
$$v=-0.05411(C_3+C_4)+0.06332i(C_3+C_4),$$
$$w=-0.05849(C_5+C_6)+0.02534i(C_5-C_6).$$

Here

$$C_i=\cos\mathbf{k}\cdot\mathbf{r}_i,$$

where the vectors $\mathbf{r}_i$ are given by

$$\mathbf{r}_i=(a/2)(1,1,0),\qquad \mathbf{r}_2=(a/2)(1,-1,0),$$
$$\mathbf{r}_3=(a/2)(1,0,1),\qquad \mathbf{r}_4=(a/2)(1,0,-1),$$
$$\mathbf{r}_5=(a/2)(0,1,1),\qquad \mathbf{r}_6=(a/2)(0,1,-1)$$

measured relative to the crystal (x, y, z) axes, and where the nearest-neighbor distance is $R=\sqrt{2}a$, so that a is the length of the edge of the fcc cell.