V is the same for MnF_2 then (55) predicts the intensity of the first-order line to be only $\frac{1}{10}$ that of the second-order peak.

V. CONCLUSION

To the methods for studying spin waves—neutron scattering, infrared absorption, optical sideband absorption—has been added another: inelastic light scattering. In the above paper we have presented the theory for both one- and two-magnon light scattering and have explained our experimental results in MnF_2 and FeF_2. It was shown that details of the magnon dispersion relation could be extracted from the spectra of scattered light. We should note that for the D_{2h}^{12} materials the selection rules for two-magnon scattering, two-magnon absorption, and optical-magnon sidebands are all different—so the experimental methods are complementary. We should also note that the ability to study magnons at the zone center and the zone edge in the same experiment is best suited to light scattering. In at least one case—NiF_2—studies of zone-edge magnons by two-magnon absorption are not possible due to a strong infrared-active phonon (E_u) at $\sim$225 cm^{-1}. However, since this phonon is not Raman active, it has not interfered with the study of the zone-edge magnon by second-order light scattering.[6]

All of the magnetic materials thus far examined by light scattering have quite simple magnon branches. But as techniques improve and experience grows it is quite likely that the use of light scattering will become much more important in the study of magnetic materials.

ACKNOWLEDGMENTS

We are grateful to J. P. Hurrell and S. P. S. Porto for helpful comments and suggestions and to C. A. Lambert for computer assistance. We also thank H. J. Guggenheim for the excellent samples of MnF_2 and FeF_2, H. L. Carter and D. H. Olson for technical assistance, A. Albert for crystal polishing and M. B. Graifman for advice on the temperature control system. We are indebted to Professor T. Moriya for a report of his theory of magnon scattering prior to publication.

PHYSICAL REVIEW VOLUME 166, NUMBER 2 10 FEBRUARY 1968

Spin-Lattice Interaction in UO_2. I. Ground-State and Spin-Wave Excitations

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A microscopic theory of the effect of spin-lattice interaction on the ground-state and spin-wave excitations in UO_2 is presented. Three parameters required by a Jahn-Teller description of the local spin-lattice interactions and an exchange constant are introduced as basic variables to describe the system at $T=0°K$. The spin-lattice ground state reveals a competition between the Jahn-Teller forces and the exchange energy that results in a reduction of the magnitude of the spin. It is also shown that the indirect quadrupole-quadrupole interaction caused by the virtual exchange of an optical phonon is as large as the exchange coupling ($\sim$30°K), and significantly modifies the spin-wave energies and wave functions. Values for the interaction parameters are obtained by fitting the theory to the excitation spectra and to wave functions deduced from far-infrared absorption spectroscopy and from the inelastic scattering of neutrons. The theory is consistent with the upper limits placed on the lattice distortion and with the anomolous behavior of the elastic constant C_{44}.

I. INTRODUCTION

THE ground-state degeneracy of a concentrated system of magnetic ions at $T=0°K$ is usually lifted by the exchange interaction. However, if the single-ion ground state is orbitally degenerate and possesses an even number of electrons, interesting alternatives to the exchange splitting may occur. These usually manifest themselves as electrostatic quadrupole-quadrupole interactions or cooperative Jahn-Teller distortions. The electrostatic interactions appear to be comparable with the exchange interaction in the rare-earth[1] and probably the actinide-series insulators. Uranium dioxide appears to be a particularly striking example of this situation. The ground-state degeneracy is largely due to the unquenched orbital motion of the two $5f$ electrons and there is evidence that the interaction between the spin and the lattice is as strong as the exchange interaction between pairs.[2,3]

In the present paper a microscopic theory of the ground electronic state and elementary electronic excitations (spin waves) is described. The basic interaction between the local spin and the distortion of the nearby lattice is parametrized by a set of constants prescribed

[1] R. J. Birgeneau, M. T. Hutchings, and R. N. Rogers, Phys. Rev. Letters **16**, 584 (1966); R. Finkelstein and A. Mencher, J. Chem. Phys. **21**, 472 (1952); B. Bleaney, Proc. Phys. Soc. (London) **77**, 113 (1961); J. M. Baker and A. F. Mau, Can. J. Phys. **45**, 403 (1967).

[2] G. Dolling and R. A. Cowley, Phys. Rev. Letters **16**, 683 (1966).

[3] O. G. Brandt and C. T. Walker, Phys. Rev. Letters **18**, 11 (1967).

by the Jahn-Teller theorem. These constants in addition to the exchange constant provide a basic set of parameters in which to describe both the ground state (lattice distortion, and spin magnitude and direction) and the spin waves. The parameters obtained by fitting the theory to experiment are shown to be reasonable by comparing them to values obtained from a point-charge model calculation. Of particular interest are the following observations:

1. There exists a competition between the Jahn-Teller energy and exchange energy that results in a non-fully polarized spin in the ground state.
2. The indirect quadrupole-quadrupole interactions caused by the virtual exchange of an optical phonon[4] are as large as the exchange forces in this system.

II. EXPERIMENTAL SITUATION

There exists a wealth of experimental evidence pertaining to the low-lying excitations in magnetically ordered UO_2. Frazer *et al.*[5] have determined that the magnetic structure consists of ferromagnetically aligned planes perpendicular to a cube axis. The moment in each plane is antiparallel to the moment in the neighboring planes. Although it is clear that the moment lies in the plane, the results cannot determine its direction within the plane. The structure is shown in Fig. 1. In contrast with most antiferromagnets, the transition to the ordered state is a first-order transition. Despite the strong spin-lattice interaction, no distortion of the lattice was observed ($\lesssim 0.0025$) at the Néel point, 30.8°K. (Blume has inferred from the lack of distortion that the first-order phase transition is a consequence of the electronic properties alone and has shown that if the ground state of the U^{4+} ion is in fact the Γ_1 singlet, but within reach of an exchange split-off component of the Γ_5, a first-order transition may occur.[6])

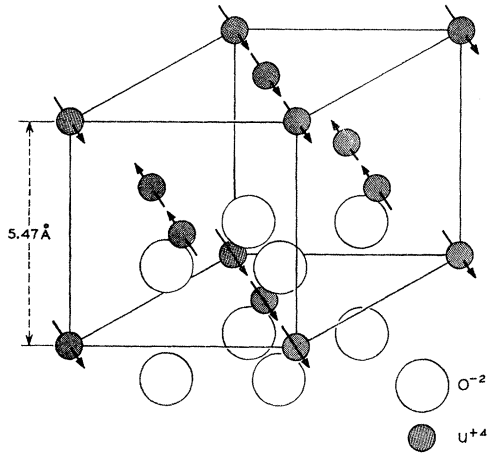

FIG. 1. Crystal structure of UO_2. Spins shown aligned along the [110] direction.

The relative dispersion of the low-lying excitations has been measured by Dolling and Cowley.[7,8] The polydomain character of the samples leads to ambiguities in the actual wave vector associated with the excitations. (This ambiguity can be resolved by a proper interpretation of the far-infrared absorption experiments.) Large differences in the transverse acoustic mode frequencies are also observed between measurements at 90 and 9°K, which directly indicate a strong coupling between the phonons and magnons.[2] The interpretation is confused, however, by the lack of understanding of the spin-wave excitations.

Relevant to the interaction between the lattice and the low-lying electronic states is the anomalous behavior of the elastic constants observed by Brandt and Walker.[3] Despite the first-order phase transition, the effects of a spin-phonon interaction are observed to persist in $C_{44} \sim 200$°K above the transition temperature. No such effect is seen for C_{11} or $C_{11}-C_{12}$. (Within the framework of the model formulated in Sec. III, these data can be used to determine the spin direction in the ferromagnetic sheet.)

Three independent measurements of the far-infrared absorption spectrum have been reported, with various interpretations.[9–11] One of the objectives of the present paper is to reveal the details of the spectra and to indicate a reasonable interpretation.

Far-Infrared Absorption

Two sources of UO_2 were used in the far-infrared absorption experiments; the first was grown by arc fusion, the second by a floating-zone technique.[12] The O/U ratio in the second was of the order of 2.005. The stoichiometry of the first is not known, but is certainly no closer to 2.0 than the second. The first sample appeared to contain more cracks and inclusions and was likely more strained than the second. Spectra were taken with a Fourier-transform spectrometer.[13]

At 4.2°K the absorption spectrum revealed the structure shown in Figs. 2–4. Only the structure in the vicinity of 17.5 cm^{-1} is sample-dependent and shown for

[4] R. Orbach and M. Tachiki, Phys. Rev. **158**, 524 (1967); J. M. Baker and A. F. Mau, Can. J. Phys. **45**, 405 (1967); D. H. McMahon and R. H. Silsbee, Phys. Rev. **135**, A91 (1964); L. K. Aminov and B. I. Kochelaev, Zh. Eksperim. i Teor. Fiz. **42**, 1303 (1962) [English transl.: Soviet Phys.—JETP **15**, 903 (1962)]; K. Sugihara, J. Phys. Soc. (Japan) **14**, 1231 (1959).

[5] B. C. Frazer, G. Shirane, D. E. Cox, and C. E. Olsen, Phys. Rev. **140**, A1448 (1965).

[6] M. Blume, Phys. Rev. **141**, 517 (1966).

[7] R. A. Cowley and G. Dolling, Bull. Am. Phys. Soc. **11**, 109 (1966).

[8] R. A. Cowley and G. Dolling, Phys. Rev., (to be published).

[9] K. Aring and A. J. Sievers, J. Appl. Phys. **38**, 1496 (1967).

[10] M. R. Daniel, Phys. Letters **22**, 131 (1966).

[11] S. J. Allen, Jr., J. Appl. Phys. **38**, 1478 (1967).

[12] A. T. Chapman and G. W. Clark, J. Am. Ceram. Soc. **48**, 494 (1965).

[13] P. L. Richards, J. Opt. Soc. Am. **54**, 1474 (1964).

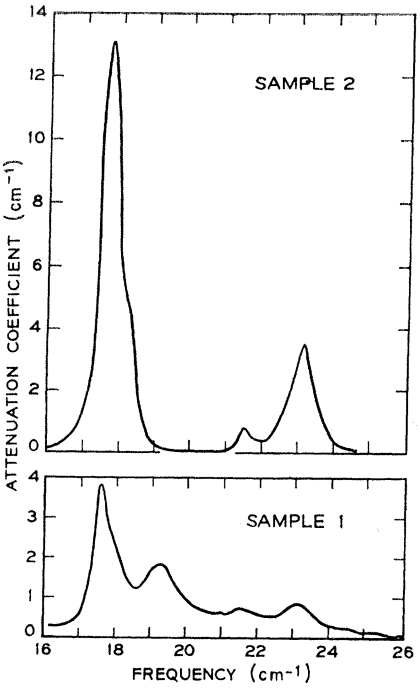

FIG. 2. Far-infrared absorption near 17 cm^{-1}. Resolution 0.2 cm^{-1}. Sample 1 grown by arc fusion, sample 2 by floating-zone technique.

both samples. As the sample is warmed, the mode frequency (17.6 cm^{-1} for sample 1 and 17.75 cm^{-1} for sample 2) does not change, but the intensity decreases and the structure broadens, so that by 20°K the line is no longer observed. The best-resolved field dependence is observed with the field parallel to a ⟨111⟩ direction. It reproduces the results obtained by Aring and Sievers.[9] The important result is the fact that the intensity of the line varies by a factor of 3 between the two samples, indicating that it is not intrinsic to pure, single-domain UO_2. In other words, the structure near 17.5 cm^{-1} cannot be a $k=0$ antiferromagnetic resonance. Furthermore, the observed frequency, 17.7±0.1 cm^{-1}, does not coincide with the 19±0.6-cm^{-1} excitation observed by inelastically scattering neutrons at a magnetic Bragg reflection.[7] Therefore, we conclude that the 19±0.6-cm^{-1} excitation observed by Cowley and Dolling[7,8] must be a zone-boundary excitation. There are two possible explanations for the 17.6-cm^{-1} structure seen in the far-infrared work—either an electric dipole electronic impurity mode or a magnetic dipole transition associated with the presence of domain walls. A magnetic dipole impurity mode could generate the observed intensity only if it were present in relatively large concentrations. The "impurity" that may be present in such large concentrations is the domain wall. It may be related to the sample-dependent weak ferromagnetism reported by Hambourger and Marcus[14] and Tourov.[15]

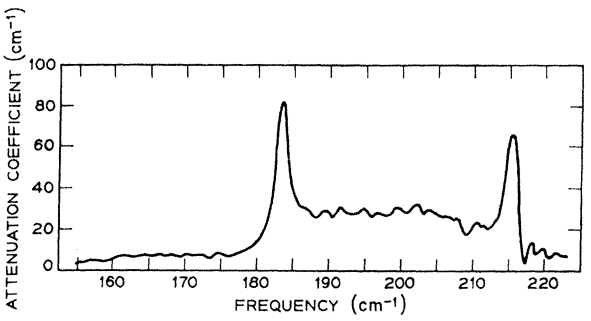

FIG. 3. Far-infrared lattice absorption appearing only in the ordered state; resolution 1 cm^{-1}.

The other absorption structure that will be discussed only briefly is that shown in Fig. 3. Allen[11] reported resonant absorption at 184 and 216 cm^{-1}, but more careful measurement of the profile has revealed a more interesting line shape. As previously discussed,[11] the structure is insensitive to fields up to 50 kG, and loses intensity without broadening or shifting as the sample approaches the Néel point. The fact that the absorption is insensitive to sublattice magnetization suggests that the transition leaves the ground electronic state unmolested—a phonon absorption. The peculiar line shape and the coincidence of the two peaks with twice the zone-boundary phonon frequencies at [001] (M_5', 109±2 cm^{-1}) and [111] (L_3', 92±1 cm^{-1})[16] suggest a two-phonon absorption allowed only in the ordered state by virtue of the spin-wave phonon coupling.

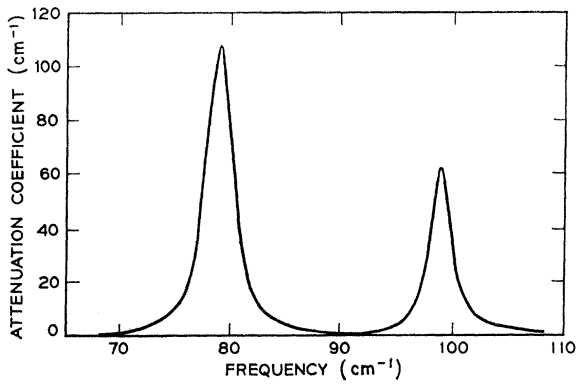

FIG. 4. Spin-wave resonance of 4.2°K; resolution 1 cm^{-1}.

The two remaining resonances at 79 and 99 cm^{-1} agree within experimental error with the modes measured by Cowley *et al.*[7,8] at a magnetic Bragg reflection; therefore, they are true $k=0$ excitations. A 50-kG field

[14] P. D. Hambourger and J. A. Marcus, Phys. Rev. **157**, 438 (1967).
[15] E. Tourov, Compt. Rend. **252**, 3420 (1961).
[16] G. Dolling, R. A. Cowley, and A. D. B. Woods, Can. J. Phys. **43**, 1397 (1965).

along either the ⟨100⟩, ⟨110⟩, or ⟨111⟩ produces only slight (<0.5 cm^{-1}) shifts and/or line broadening. The temperature dependences of the frequencies and linewidths are shown in Fig. 5. At ~25°K, the frequencies have fallen by ~5%, approximately the change in sublattice magnetization.[5] From 4.2 to 25°K, the total integrated intensity, within experimental error, does not change. One concludes that these modes are the two antiferromagnetic resonances that one expects for a two-sublattice antiferromagnet.

Little more than a qualitative fit to experiment can be achieved with an exchange-coupled[17] two-sublattice model. Consider, for example, the fit suggested by Allen.[11] The relative intensities of the high-to-low frequency mode are predicted to be ~1.5. The observed ratio is ~0.6±0.05. Further, the relative dispersion when compared to the observations by Cowley and Dolling[7,8] shows only qualitative agreement, differing by as much as ~80 cm^{-1} for spin waves near the zone boundary propagating perpendicular to the ferromagnetic sheets. These two deficiencies appear to be suffered by any two-sublattice model where the U^{4+}–U^{4+} interaction is dominated by exchange.[18]

Considering the results of Brandt *et al.*[3] and Dolling *et al.*,[2] it is clear that one must include the interaction with the phonons. In the next section a model is considered which modifies the spin-wave spectrum by including spin-lattice interaction and it is shown that the proper dispersion relations and wave functions can be obtained.

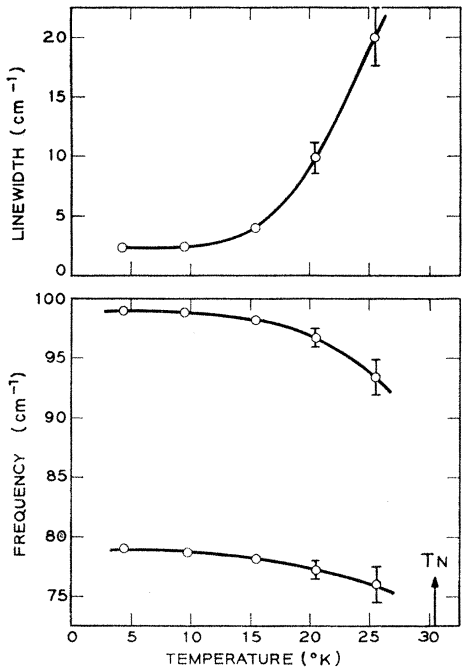

FIG. 5. Temperature dependence of frequency and linewidth of spin-wave modes.

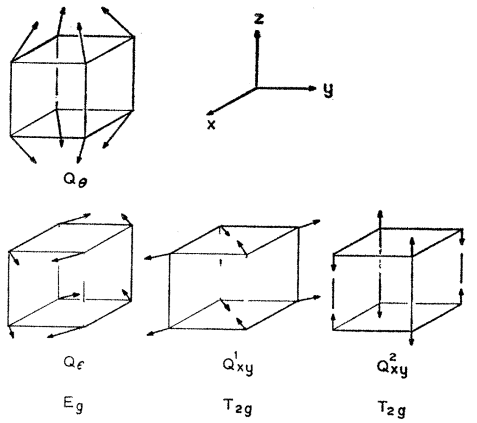

FIG. 6. Types of distortion of the cube of oxygens that mix levels of the Γ_5. Only one of the three different modes for each of the T_{2g} distortions is shown.

III. THEORY OF THE SPIN-LATTICE INTERACTION

There are clearly two aspects of the problem. The first is to find the proper ground state. In a molecular-field approximation the problem reduces to a calculation of quantum-mechanical average values and a minimization of the total free energy which includes exchange energy, spin-lattice interaction energy, and the elastic energy. Having found the ground state, the spin-wave excitations can then be calculated by introducing suitable off-diagonal ion-pair interactions. The off-diagonal terms include, in addition to the exchange coupling, indirect quadrupole-quadrupole interactions which are biquadratic in the spin but may be as large as the exchange.

The interaction between the spin and lattice distortion is assumed to occur exclusively through the crystal field (magnetostriction). Although exchange striction is also present, it will be apparent that it is too small to compete with the magnetostrictive terms. The ground electronic state of the U^{4+} ion in UO_2 is taken as the Γ_5,[19,20] and is predominantly derived from the $^3H_4$ term of the $5f^2$ configuration of the U^{4+} ion under the action of the cubal crystal field formed by the eight surrounding oxygens. The local distortions of the cube of oxygens that mix levels of the Γ_5 manifold must transform as do the representations contained in the symmetric square $[\Gamma_5^2]$ which are E_g and T_{2g}. An analysis of the various modes of distortion of the UO_8 complex reveal a single E_g mode and two T_{2g}

[17] D. ter Haar and M. E. Lines, Phil. Trans. Roy. Soc. (London) **255**, 1 (1962).

[18] Obviously anisotropies must be introduced to produce any fit at all but within the framework of the above models these terms are found to be <15% of the isotropic exchange.

[19] C. A. Hutchison Jr. and G. A. Candela, J. Chem. Phys. **27**, 707 (1957).

[20] H. U. Rahman and W. A. Runciman, J. Phys. Chem. Solids **27**, 1833 (1966).

modes shown in Fig. 6. The Wigner-Eckart theorem allows us to express the interaction in terms of three arbitrary constants which can be specified only by a more detailed examination of the problem. The matrix elements between states of the Γ_5 are written as

$$H_{ij}=\sum_{k,\mu} F_k h_{ij}(k,\mu) q_{k,\mu}, \tag{1}$$

where k runs over the three distortions E_g and $2T_{2g}$ and μ over their components. $h_{ij}(k,\mu)$ is the i,jth component of coupling coefficient[21] for the normal coordinate operator $q_{k,\mu}$ between the states i and j in the Γ_5 manifold, and F_k is the reduced matrix element. Equation (1) is clearly an expression of the Jahn-Teller effect.[22]

In order to estimate the magnitude of the F_k, we consider the interaction of the quadrupole moment on the U^{4+} with the surrounding eight O^{2-} monopoles. The electrostatic energy for small displacements of the oxygens from equilibrium is given by

$$E=(4\pi\epsilon_0)^{-1}(Ze^2/\sqrt{3}r_0^4)\langle r_e^2\rangle\langle\alpha\,||\,J\,||\,\alpha\rangle \times\sum_i\{Q[\tfrac{1}{2}O_\theta(2z_i\delta_{zi}-x_i\delta_{xi}-y_i\delta_{yi})+\tfrac{3}{2}O_\epsilon(x_i\delta_{xi}-y_i\delta_{yi})] -2P[O_{yz}(y_i\delta_{zi}+z_i\delta_{yi})+\cdots]-5P[O_{yz}x_i\delta_{yi}\delta_{xi}\delta_{zi}+\cdots]\}, \tag{2}$$

where the sum is over the eight oxygens, e is the electronic charge, Z is the charge on the O^{2-} in units of electronic charge, r_0 is the U^{4+}–O^{2-} separation, and $\langle r_e^2\rangle$ is the average square radius for the $5f$ electrons in the Γ_5 configuration. $\langle\alpha\,||\,J\,||\,\alpha\rangle$ is a reduced matrix element evaluated by Elliot and Stevens.[23] $\delta_{\alpha i}$ assumes the sign of the αth component of the vector pointing from the U^{4+} ion to the ith O^{2-} ion, while α_i is the displacement of the ith O^{2-} in the α direction. The Γ_5 triplet can be transformed into an $S=1$ manifold, in which case we write

$$O_\theta=3S_z^2-S(S+1),$$
$$O_\epsilon=S_x^2-S_y^2,$$
$$O_{\alpha\beta}=\tfrac{1}{2}(S_\alpha S_\beta+S_\beta S_\alpha). \tag{3}$$

P and Q are then determined as follows:

$$3J_z^2-J(J+1)=Q[3S_z^2-S(S+1)],$$
$$(J_\alpha J_\beta+J_\beta J_\alpha)=P(S_\alpha S_\beta+S_\beta S_\alpha). \tag{4}$$

Relating Eq. (2) to Eq. (1) we have, for instance,

$$F(E_g)=z_0Q(4\pi\epsilon_0)^{-1}(Ze^2/\sqrt{3}r_0^4)\langle r_e^2\rangle\langle\alpha\,||\,J\,||\,\alpha\rangle, \tag{5}$$

where $z_0=8$ the number of surrounding oxygens. The parameters $F_1(T_{2g})$ and $F_2(T_{2g})$ obtain in the same fashion. To estimate the interaction energy, we simply multiply $F(E_g)$ by the root-mean-square displacement of one of the oxygens due to the zero-point motion, $\sim$0.05 Å. The other parameters in (5) are estimated as follows. Using the wave functions of Hutchinson *et al.*,[19] we get $Q=4$, $P=\frac{13}{4}$. For $\langle r_e^2\rangle$, we use a value calculated by Lenander,[24] 0.471 Å^2. $r_0=2.36$ Å and $\langle\alpha\,||\,J\,||\,\alpha\rangle=0.021$.[23] The interaction energy is found to be $\sim z_0$ 7.5 cm^{-1}, a rather large interaction energy to contend with.

We rewrite the interaction energy in terms of three parameters, A, B, C:

$$E=F\sum_i A[\tfrac{1}{2}O_\theta(2z_i\delta_{zi}-x_i\delta_{xi}-y_i\delta_{yi}) +\tfrac{3}{2}O_\epsilon(x_i\delta_{xi}-y_i\delta_{yi})]+B[O_{yz}(y_i\delta_{zi}+z_i\delta_{yi})+\cdots] +C(O_{yz}x_i\delta_{xi}\delta_{yi}\delta_{zi}+\cdots), \tag{6}$$

where

$$F=(4\pi\epsilon_0)^{-1}(Ze^2/\sqrt{3}r_0^4)\langle r_e^2\rangle\langle\alpha\,||\,J\,||\,\alpha\rangle.$$

For the preceding point-charge calculation, we have $A\sim4$, $B\sim-6.5$, $C\sim-16$. In the following discussion, A, B, C are left as parameters to be determined by a good fit to experiment. However, if the fit is reasonable, they will not differ drastically from the above values estimated by the point-charge calculation. Using Eq. (6), we now calculate the electron and phonon ground state and then proceed to find the low-lying electronic excitations.

A. Ground State

To find the ground state in the molecular-field approximation, we write down the total free energy including exchange, magnetostrictive, and elastic energies. Most treatments of the magnetostriction problem proceed from a phenomenological expression of the free energy.[25] Since the lattice dynamics of UO_2 are rather well understood,[16] we elect to derive the free energy from a microscopic point of view with the aid of Eq. (6). Although the final expression must resemble the phenomenological result, the microscopic theory allows us to isolate terms due to internal distortions from those due to external strains. Ultimately, we wish to check the consistency of the theory by comparing the parameters used to fit the excitation spectrum with those used to fit the ground state. This can be done only if both are derived from the same microscopic interaction.

Assuming a homogeneous deformation, Eq. (6) can

[21] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, Mass., 1963).
[22] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).
[23] R. J. Elliot and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).
[24] C. J. Lenander, Phys. Rev. **130**, 1033 (1963).
[25] For a review of magnetostriction, see J. Kanamori, in *Magnetism I*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), p. 127.

be written in terms of internal and external strains as follows:[26]

$$E_{M-E}=(z_0r_0/\Omega_0\sqrt{3})\times FA\{\tfrac{1}{2}O_\theta(2U_{zz}-U_{xx}-U_{yy})+\tfrac{3}{2}O_\epsilon(U_{xx}-U_{yy})\}+(z_0r_0/\Omega_0\sqrt{3})FB\{O_{yz}(U_{zy}+U_{yz})+\cdots\}+(z_0/2\Omega_0)FC\{O_{yz}[u_x(1)-u_x(2)]+\cdots\},\quad(7)$$

where in the Voigt notation we can substitute $U_{xx}=S_1$, $\cdots$, and $U_{yz}+U_{zy}=S_4$, etc. $\bar{u}(1)$ and $\bar{u}(2)$ are the internal displacements of either oxygen 1 or oxygen 2 with respect to the uranium. Ω_0 is the volume of the paramagnetic unit cell and E_{M-E} is clearly the energy per unit volume.

The elastic energy for a nonprimitive lattice[27] is written as

$$E_E=\tfrac{1}{2}\sum_{k\alpha}\sum_{k'\beta}\begin{Bmatrix}k & k'\\ \alpha & \beta\end{Bmatrix}u_\alpha(k)u_\beta(k')+\sum_{k\alpha}\sum_{\rho}\begin{Bmatrix}k\\ ,\\ \alpha\end{Bmatrix}\begin{matrix}\\ \rho\\ \\ \end{matrix}u_\alpha(k)S_\rho+\tfrac{1}{2}\sum_{\rho\sigma}\{\rho\sigma\}S_\rho S_\sigma;\quad(8)$$

before introducing the exchange energy we first combine (7) and (8) and find the equilibrium lattice distortion for a given set of quadrupole moments. The addition of Eq. (7) to (8) introduces the following linear terms in the expression for elastic energy:

$$\sum_{k,\alpha}\lambda_\alpha{}^k u_\alpha(k)+\sum_\rho\gamma_\rho S_\rho.\quad(9)$$

For a given external strain the elastic energy is minimized with respect to the internal distortions by the internal distortion

$$u_\alpha(k)=-\sum_\rho\sum_{k'\beta}\begin{pmatrix}k' & k\\ \beta & \alpha\end{pmatrix}^{-1}\begin{pmatrix}k'\\ ,\\ \beta\end{pmatrix}\begin{matrix}\\ \rho\\ \\ \end{matrix}S_\rho-\sum_{k'\beta}\begin{pmatrix}k' & k\\ \beta & \alpha\end{pmatrix}^{-1}\lambda_\beta{}^{k'}.\quad(10)$$

The total elastic energy then becomes, upon substitution of (10) into Eqs. (7) and (8),

$$E_E+E_{M-E}=\tfrac{1}{2}\sum_{\rho\rho'}C_{\rho\rho'}S_\rho S_{\rho'}-\tfrac{1}{2}\sum_{k\alpha}\sum_{k'\beta}\lambda_\alpha{}^k\begin{pmatrix}k' & k\\ \beta & \alpha\end{pmatrix}^{-1}\lambda_\beta{}^{k'}\times\sum_\rho\left[\gamma_\rho-\sum_{k'\beta}\sum_{k\alpha}\lambda_\beta{}^{k'}\begin{pmatrix}k & k'\\ \alpha & \beta\end{pmatrix}^{-1}\begin{pmatrix}k\\ ,\\ \alpha\end{pmatrix}\begin{matrix}\\ \rho\\ \\ \end{matrix}\right]S_\rho.\quad(11)$$

We now have an equation that can be simply minimized with respect to the external strains $\{S_\rho\}$ and the total gain in energy for a given set of quadrupole moments calculated.

The parameters needed to evaluate the matrices in Eq. (11) are taken from the best rigid-ion model proposed by Dolling *et al.*[16] Although the shell model is clearly a better model for the lattice dynamics, we are not inclined to include these complications at this time. The short-range force contributions are straightforwardly calculated from the definition of the matrices.[28] The Coulomb contributions are obtained by reference to calculations by Srinivasan.[28] In particular, we find

$$\sum_\rho\sum_{k'\beta}\sum_{k,\alpha}\lambda_\beta{}^{k'}\begin{pmatrix}k & k'\\ \alpha & \beta\end{pmatrix}\begin{pmatrix}k\\ ,\\ \alpha\end{pmatrix}\begin{matrix}\\ \rho\\ \\ \end{matrix}S_\rho=\Omega_0^{-1}(z_0r_0FCG/H)(\langle O_{yz}\rangle S_4+\langle O_{xz}\rangle S_5+\langle O_{xy}\rangle S_6)\quad(12)$$

and

$$\sum_\rho\gamma_\rho S_\rho=\Omega_0^{-1}(z_0r_0FB/\sqrt{3})\times(\langle O_{yz}\rangle S_4+\langle O_{xz}\rangle S_5+\langle O_{xy}\rangle S_6)+\Omega_0^{-1}(z_0r_0FA/\sqrt{3})\times[\langle O_\theta\rangle S_3+(\tfrac{3}{2}\langle O_\epsilon\rangle-\tfrac{1}{2}\langle O_\theta\rangle)S_1-(\tfrac{3}{2}\langle O_\epsilon\rangle+\tfrac{1}{2}\langle O_\theta\rangle)S_2],\quad(13)$$

where the new parameters G and H are given by

$$G=(2/\sqrt{3})[10.076Z^2+\tfrac{2}{3}(A_1-B_1)],$$
$$H=\tfrac{4}{3}(A_1+2B_1)+4(A_2+2B_2).\quad(14)$$

The constants A_1, B_1, A_2, and B_2 are short-range force parameters defined by and obtained from Dolling *et al.*[16] The external strains that minimize the free energy for a given set of quadrupole moments are

$$S_1=\tfrac{1}{2}(\langle O_\theta\rangle-3\langle O_\epsilon\rangle)[z_0r_0FA/\sqrt{3}\Omega_0(C_{11}-C_{12})],$$
$$S_2=\tfrac{1}{2}(\langle O_\theta\rangle+3\langle O_\epsilon\rangle)[z_0r_0FA/\sqrt{3}\Omega_0(C_{11}-C_{12})],$$
$$S_3=-\langle O_\theta\rangle[z_0r_0FA/\sqrt{3}\Omega_0(C_{11}-C_{12})],$$
$$S_{4,5,6}=-(z_0r_0F/\Omega_0C_{44})[(B/\sqrt{3})-(G/H)C]\langle O_{yz,xz,xy}\rangle,\quad(15)$$

where the quadrupole parameters are quantum-mechanical averages. The change in energy per unit volume is

$$\Delta(E_E+E_{M-E})=-\tfrac{1}{2}(4\pi\epsilon_0/e^2r_0^2)[(z_0FCr_0)^2/2H]\times(\langle O_{xy}\rangle^2+\langle O_{xz}\rangle^2+\langle O_{yz}\rangle^2)-\tfrac{1}{2}\Omega_0^{-1}[(z_0r_0F)^2/C_{44}\Omega_0]\times[(B/\sqrt{3})-(G/H)C]^2(\langle O_{xy}\rangle^2+\langle O_{xz}\rangle^2+\langle O_{yz}\rangle^2)-\tfrac{1}{2}\Omega_0^{-1}[(z_0r_0FA)^2/2(C_{11}-C_{12})\Omega_0](3\langle O_\epsilon\rangle^2+\langle O_\theta\rangle^2).\quad(16)$$

[26] W. F. Brinkman (unpublished).

[27] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 129 ff.

[28] R. Srinivasan, Proc. Phys. Soc. (London) **72**, 566 (1958).

To have the total magnetoelastic energy in the molecular-field approximation, we simply add to (16)

$$E_M=-\tfrac{1}{2}\Omega_0^{-1}z_uJ\langle\bar{S}\rangle^2, \tag{17}$$

where J is the exchange constant and $z_u=4$ is the effective number of spins contributing to the molecular field.

To minimize the total energy, a single-ion ground-state wave function is constructed from an arbitrary mixture of the components of the Γ_5. The sum of expressions (16) and (17) is then minimized with respect to this wave function.

Consider the wave function

$$|\ \rangle=\alpha_x\,|\,yz\rangle+\alpha_y\,|\,xz\rangle+\alpha_z\,|\,yx\rangle, \tag{18}$$

where the basis functions are real. The plane containing the spin direction will be taken as the xy plane. Since there is no spin in the z direction, we restrict the wave function to have the phase of α_x equal to the phase of α_y. Then $\alpha_x=|\,\alpha_x\,|\exp(i\varphi)$, $\alpha_y=|\,\alpha_y\,|\exp(i\varphi)$, and α_z can be taken as real. We then write

$$\begin{aligned}|\ \rangle=&\sin\theta\cos\xi\exp(i\varphi)\,|\,yz\rangle\\&+\sin\theta\sin\xi\exp(i\varphi)\,|\,xz\rangle+\cos\theta\,|\,xy\rangle.\end{aligned} \tag{19}$$

The average spin and quadrupole components are

$$\begin{aligned}\langle S^x\rangle&=\sin\xi\sin2\theta\sin\varphi,\\\langle S^y\rangle&=\cos\xi\sin2\theta\sin\varphi,\\\langle S^z\rangle&=0,\\\langle O_{yz}\rangle&=\tfrac{1}{2}\sin2\theta\cos\varphi\sin\xi,\\\langle O_{xz}\rangle&=\tfrac{1}{2}\sin2\theta\cos\varphi\cos\xi,\\\langle O_{xy}\rangle&=\tfrac{1}{2}\sin2\xi\sin^2\theta,\\\langle O_\theta\rangle&=(1-3\cos^2\theta),\\\langle O_\epsilon\rangle&=-\sin^2\theta(\cos^2\xi-\sin^2\xi).\end{aligned} \tag{20}$$

As a function of φ, ξ, and θ, the free energy becomes

$$\begin{aligned}E=&-\tfrac{1}{2}\epsilon_1(\sin^22\theta\sin^2\varphi)-\tfrac{1}{8}\epsilon_2(\cos^2\varphi\sin^22\theta+\sin^22\xi\sin^4\theta)\\&-\tfrac{1}{2}\epsilon_3[(1-3\cos^2\theta)^2+3\sin^4\theta\cos^22\xi],\end{aligned} \tag{21}$$

where

$$\begin{aligned}\epsilon_1&=\Omega_0^{-1}z_uJ,\\\epsilon_2&=\Omega_0^{-1}\left[\frac{4\pi\epsilon_0\Omega_0}{e^2r_0^2}\frac{(z_0r_0FC)^2}{2H}+\frac{(z_0r_0F)^2}{C_{44}\Omega_0}\left(\frac{B}{\sqrt{3}}-\frac{G}{H}C\right)^2\right],\\\epsilon_3&=\Omega_0^{-1}[(z_0r_0FA)^2/2(C_{11}-C_{12})\Omega_0].\end{aligned} \tag{22}$$

First, consider the minimum of E with respect to φ. $\varphi=0$ or $\tfrac{1}{2}\pi$ as $4\epsilon_1<\epsilon_2$ or $4\epsilon_1>\epsilon_2$. The state $\varphi=0$ possesses no average spin and corresponds to an ordered quadrupole structure. Since UO_2 is an antiferromagnet, we require $\varphi=\tfrac{1}{2}\pi$ and $4\epsilon_1>\epsilon_2$. The minimum with respect to ξ is either $\xi=0$ or $\xi=\tfrac{1}{4}\pi$, as $\epsilon_2<12\epsilon_1$ or $\epsilon_2>12\epsilon_1$. That is to say the spin direction is either along a $\langle010\rangle$ direction or $\langle110\rangle$ direction, depending on whether the quadrupole interacts strongest with the compressional strains or shear strains, respectively. The elastic constant data of Brandt and Walker[3] indicates a softening of the shear elastic constant C_{44} approximately 200°K above the phase transition. The softening increases as the temperature is reduced until the system finally orders at 30°K. This is not observed for C_{11}–C_{12} or C_{11}. The behavior is consistent with acoustic wave interaction with a concentrated system of Jahn-Teller active ions, with the interaction dominated by the B and C terms in Eq. (6), either B or C or both are much greater than A. It follows then that $\epsilon_2\gg\epsilon_3$ and the spin alignment must be along a $\langle110\rangle$ direction. We are left with $\xi=\tfrac{1}{4}\pi$, $\varphi=\tfrac{1}{2}\pi$, therefore, $\langle S^x\rangle=\langle S^y\rangle=(1/\sqrt{2})\sin2\theta$, $\langle O_{xz}\rangle=\langle O_{yz}\rangle=\langle O_\epsilon\rangle=\langle S_z\rangle=0$, $\langle O_{xy}\rangle=\tfrac{1}{2}\sin^2\theta$, and $\langle O_\theta\rangle=(1-3\cos^2\theta)$.

Before minimizing E with respect to θ, we transform to a new angle θ' defined by

$$\theta'=\theta-\tfrac{1}{4}\pi,$$

then

$$\begin{aligned}E=&-\tfrac{1}{2}\epsilon_1\cos^22\theta'-\tfrac{1}{2}\epsilon_2\times\tfrac{1}{16}(1+\sin2\theta')^2\\&-\tfrac{1}{2}\epsilon_3\times\tfrac{1}{4}(1-3\sin2\theta')^2.\end{aligned} \tag{23}$$

The minimum with respect to θ' is found at

$$\sin2\theta'=(\epsilon_2-12\epsilon_3)/(16\epsilon_1-\epsilon_2-36\epsilon_3). \tag{24}$$

It is interesting to note that the ground state, which can be written as $\cos\theta'\,|\,+1\rangle-\sin\theta'\,|\,-1\rangle$ (where the axis of quantization is taken to be $\langle110\rangle$), is not a fully aligned state; the average spin value differs from 1 by $(1-\cos2\theta')$. This is simply a consequence of the competition between the magnetoelastic energy and the exchange energy. Further, if the interactions with the lattice are sufficiently large, $\epsilon_2+12\epsilon_3>8\epsilon_1$, a purely quadrupole state will be favored. This is clearly not the case in UO_2.[5,29] Competition between a cooperative Jahn-Teller distortion and ordered spin state is expected whenever the ground electronic state possesses a large degree of orbital degeneracy. The interesting case where the ordered quadrupole state is favored may be relevant in other systems. The observations of Varsanyi on $PrCl_3$ suggest that, at sufficiently low temperatures, the degeneracy of the non-Kramers ground state may be lifted by an ordering of quadrupoles.[30]

Before proceeding to the calculation of the spin-wave excitations, we write down the wave functions for both

[29] Although neutrons can be Bragg scattered from an array of electronic quadrupoles, the cross section is down by at least two orders of magnitude from the cross section for scattering from an array of magnetic moments. Furthermore, in the above calculation, the quadrupole structure formed would be commensurate with paramagnetic lattice and hence generate no new Bragg peaks.

[30] F. L. Varsanyi, Bull. Am. Phys. Soc. **12**, 295 (1967); and (unpublished).

spin sites as follows:

$$|g_+\rangle=|+1\rangle\cos\theta'-|-1\rangle\sin\theta',$$
$$|g_-\rangle=|-1\rangle\cos\theta'-|+1\rangle\sin\theta',$$
$$|a_+\rangle=|0\rangle,$$
$$|a_-\rangle=|0\rangle,$$
$$|b_+\rangle=|+1\rangle\sin\theta'+|-1\rangle\cos\theta',$$
$$|b_-\rangle=|+1\rangle\cos\theta'+|-1\rangle\sin\theta'. \quad (25)$$

The molecular-field splittings are given by the following spin Hamiltonian:

$$-z_uJ\langle S_z'\rangle S_z'-\delta(S_z'^2-S_x'^2)+\eta[3S_y'^2-S(S+1)]. \quad (26)$$

The corresponding splittings are $z_uJ+3z_uJ\sin2\theta'+6\eta$ for the energy between the ground state and first excited state and $2z_uJ$ for the separation of the ground state and the reversed spin state $|b_+\rangle$ or $|b_-\rangle$. z_u is equal to the number of nearest-neighbor uranium ions in a given plane perpendicular to the cube axis and is equal to 4. Since η arises from the interaction with the compressional strains and δ from the interaction with shears, we expect η to be small compared with δ.

B. Spin-Wave Excitations

The spin-wave excitations can be obtained by introducing those off-diagonal spin and quadrupole components which couple excitations to the $|a\rangle$ state on site i to a similar excitation on a neighboring lattice site j. One of the coupling terms is the isotropic exchange represented as $J\mathbf{S}_i\cdot\mathbf{S}_j$. We wish to also show that there exists an indirect quadrupole-quadrupole interaction which is as strong as the exchange coupling.

The interaction that is calculated is essentially the quadrupole coupling produced by the virtual exchange of a phonon.[4] Physically, a change in quadrupole moment at site i causes the neighboring lattice to distort via the interaction in Eq. (6). The energy is minimized if the surrounding quadrupoles also change in a manner determined by the geometry of the lattice and character of the quadrupole-lattice interaction. This clearly leads to a quadrupole-quadrupole interaction which must have a form similar to the electrostatic interaction but with coefficients which may be decidedly different. Whereas previous treatments have considered only the interaction of the quadrupole with the acoustic phonons, we consider the optical-phonon interaction to be important; indeed, the relative displacements of the oxygen ions with respect to the uranium ion interact with the quadrupole.

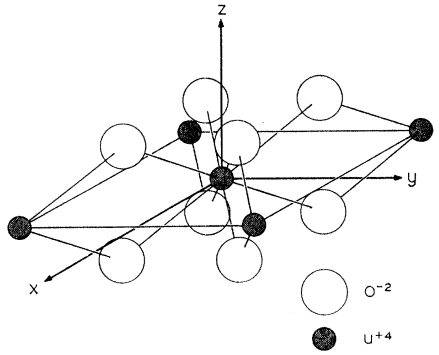

FIG. 7. The xy plane showing the oxygen ions, uranium ions, and coordinate system used in Eq. (28).

The problem is simplified by approximating the optical modes with an Einstein model. We consider that an individual oxygen ion vibrates independent of the rest of the lattice, inside the tetrahedron of the four surrounding uranium ions. From the force constants, this frequency is found to be ~300 cm^{-1}. The off-diagonal interaction of the quadrupole with these modes is removed in second-order perturbation theory. A pair of terms such as aO_ix+bO_jx, where x is the displacement of the oxygen ion in question, simply contribute

$$-2ab(\hbar/2m\omega)^{1/2}(\hbar\omega)^{-1}O_iO_j \quad (27)$$

to the interaction Hamiltonian. ω is the frequency of oscillation of the oxygen ion and m its mass. The coefficients a and b are easily extracted from Eq. (6). The interaction of the quadrupole back on itself simply shifts the entire Γ_5 manifold and does not produce any interesting effects. This approach cannot be used as an alternative to the preceding calculation for the ground state. For instance, substituted into expressions like (27), diagonal or average values of the quadrupole operator will not even give the correct sign for the dependence of magnetoelastic energy on relative quadrupole orientation. This is due to the fact that we have, essentially, forced the external strains to be zero when calculating the off-diagonal terms.

Carrying out this prescription using Eq. (6), we calculate the following quadrupole-quadrupole interaction between a single U^{4+} ion and its four neighbors. Figure 7 shows the coordinate system and relevant oxygen ions. The interaction energy is

$$H_{xy}=-u_0\sum_j\{A^2O_{\theta i}O_{\theta j}-9A^2O_{\epsilon i}O_{\epsilon j}+2(C^2-2B^2)O_{xyi}O_{xyj}$$
$$+\delta_{xj}\delta_{yj}([O_{yzi}O_{xzj}+O_{xzi}O_{yzj}]2C^2$$
$$+2A[B+C][O_{\theta i}O_{xyj}+O_{\theta j}O_{xyi}])\}, \quad (28)$$

where $\delta_{\alpha j}$ assumes the sign of the αth component of the vector pointing from i to j. The energy u_0 is given as

$$u_0=2F^2(\hbar/2m\omega)(\hbar\omega)^{-1} \quad (29)$$

and has the numerical value of ~0.048 cm^{-1}. For the point-charge model the term $2(C^2-2B^2)u_0=17$ cm^{-1}, demonstrating that the effective interaction is expected

to be of the same order of magnitude as the exchange. It is instructive to consider the magnitude of the similar term arising from the purely electrostatic interaction. It is found to be ~ 1 cm^{-1}. The enhancement of the indirect quadrupole-quadrupole interaction is very approximately given by $r^5_{U\text{-}U}\alpha/r^8_{U\text{-}O}$, where α is the polarizability of the OU_4 complex. The uranium-uranium distance $r_{U\text{-}U}$ is approximately $1.6\times r_{U\text{-}O}$, the oxygen-uranium distance, and the polarizability is approximately $r^3_{U\text{-}O}$, indicating that most of the enhancement arises from the reduced separation involved in uranium-oxygen interaction.

The quadrupole interaction with the other nearest neighbors in the yz and xz planes is found in an analogous way or by simply performing suitable rotation transformations on (28). The complete interaction Hamiltonian is constructed by extracting from the quadrupole and exchange interactions the *off-diagonal* components that couple spin deviations on one site to those on the next. Essential to the discussion is the use of the molecular-field ground state (25) rather than the fully polarized spin state. This significantly modifies the off-diagonal spin and quadrupole operators. Transforming to a plane-wave representation and writing the Hamiltonian in second quantized form we have

$$\begin{aligned}H=&\sum_q R(q)\,(a_q^\dagger a_q+b_q^\dagger b_q)+S(q)\,(a_q b_{-q}+a_q^\dagger b_{-q}^\dagger)\\&+T(q)\,(a_q b_q^\dagger+a_q^\dagger b_q)\\&+\tfrac{1}{2}V(q)\,(a_q a_{-q}+a_q^\dagger a_{-q}^\dagger+b_q b_{-q}+b_q^\dagger b_{-q}^\dagger),\end{aligned}\tag{30}$$

where

$$\begin{aligned}R(q)=&z_uJ+3z_uJ\sin2\theta'+6\eta+\gamma_1(q)\\&\times[z_uJ+\tfrac{9}{2}(z_uA^2u_0)\,(1+\sin2\theta')]\\&+\tfrac{1}{4}(z_uC^2u_0)\,(1-\sin2\theta')\gamma_2(q),\\S(q)=&[2z_uJ+\tfrac{1}{4}(z_u(C^2-2B^2))u_0(1-\sin2\theta')]\gamma_3(q),\\T(q)=&-[2z_uJ\sin2\theta'+\tfrac{1}{4}z_u(C^2-2B^2)u_0\\&\times(1-\sin2\theta')]\gamma_3(q),\\V(q)=&[\tfrac{9}{2}(z_uA^2u_0)\,(1+\sin2\theta')-z_uJ\sin2\theta']\gamma_1(q)\\&-\tfrac{1}{4}(z_uC^2u_0)\,(1-\sin2\theta')\gamma_2(q),\end{aligned}\tag{31}$$

$$\begin{aligned}\gamma_1(q)=&\cos\tfrac{1}{2}(q_xa)\,\cos\tfrac{1}{2}(q_ya),\\\gamma_2(q)=&\sin\tfrac{1}{2}(q_xa)\,\sin\tfrac{1}{2}(q_ya),\\\gamma_3(q)=&\cos\tfrac{1}{2}(q_za)\,\cos\tfrac{1}{4}[(q_x+q_y)a]\cos\tfrac{1}{4}[(q_x-q_y)a].\end{aligned}\tag{32}$$

a is the cubic unit cell dimension, 5.47 Å. The Brillouin zone is shown in Fig. 8. The Hamiltonian (30) is valid only along the symmetry directions denoted by dashed lines in the figure. At a general point in q space additional terms are introduced which complicate the system but they need not be discussed here.

The Hamiltonian can be easily diagonalized using the equation-of-motion technique.[31] The eigenfrequencies are found to be

$$\begin{aligned}\lambda_+^2&=(R+T)^2-(V+S)^2,\\\lambda_-^2&=(R-T)^2-(V-S)^2.\end{aligned}\tag{33}$$

Of particular interest is the ratio of the intensities seen in a far-infrared absorption. If we define $\sin\theta_+=(V+S)/(R+T)$ and $\sin\theta_-=(V-S)/(R-T)$, the intensity ratio becomes

$$\frac{I_+}{I_-}=\frac{\lambda_+}{\lambda_-}\frac{1-\tan\frac{1}{2}\theta_+}{1+\tan\frac{1}{2}\theta_+}\frac{1-\tan\frac{1}{2}\theta_-}{1+\tan\frac{1}{2}\theta_-}\frac{1-\sin2\theta'}{1+\sin2\theta'},\tag{34}$$

where θ' is the parameter determined from the ground-state calculation.

The theory is reconciled with experiment by fitting the spectrum of spin-wave excitations to the values at Γ measured by the far-infrared absorption and at X, Z, and M measured by neutron scattering.[7,8] In addition, we require that the theory predict the ratio of intensities of the lines seen in the far-infrared absorption experiments. The input parameters are $\lambda^+(\Gamma)=99$ cm^{-1}, $\lambda^-(\Gamma)=79$ cm^{-1}, $\lambda(X)=19.6$ cm^{-1}, $\lambda(Z)=97$ cm^{-1}, $\lambda(M)=85$ cm^{-1}, and $I^+/I^-=0.6$. The frequencies can be fit with little difficulty. The best fit to the ratio of far-infrared intensities, and still obtain reasonable parameters, is found to be ~ 0.75, a considerable improvement over the exchange-dominated spin-wave models,[11] which gave ratios of ~ 1.5. The resulting spin-wave dispersion is shown in Fig. 9. In return we extract the following interaction parameters: $\sin2\theta'=0.375$, $z_uJ=35$ cm^{-1}, $|A|=1.5$, $|B|=31.5$, $|C|=31$, $\eta=-2.2$ cm^{-1}, and $\delta=32$ cm^{-1}. The largest quadrupole

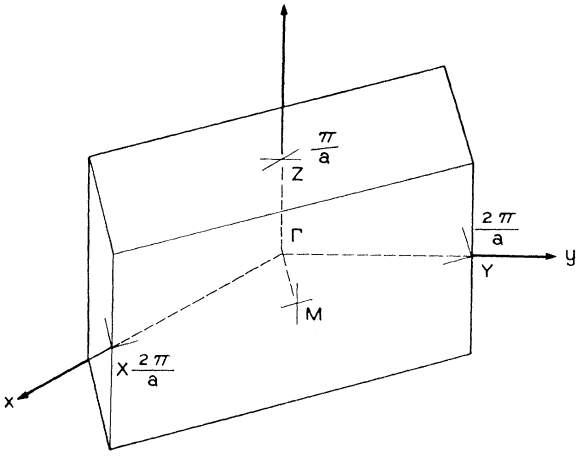

FIG. 8. The magnetic Brillouin zone. The dashed lines are the regions where the Hamiltonian in the text is valid.

[31] S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum Press, Inc., New York, 1967), p. 97 ff.

interaction term $\frac{1}{4}[z_u u_0(C^2-2B^2)](1-\sin 2\theta')$ is ~ 31 cm^{-1}, of the same order as the exchange energy.

Clearly, the problem is overspecified; for there are only four basic parameters: A, B, C, and J. The quantities $\sin 2\theta'$ and η can also be determined from the ground-state calculation and expressed in terms of A, B, C, and J. If the theory is to be self-consistent the following must hold.

1. A, B, and C should not differ seriously from the results of the point-charge calculation.
2. From the behavior of the elastic constants we have that B and C should be $\gg A$ and $\delta \gg \eta$.
3. The values of $\sin 2\theta'$ and η extracted from the fit and those calculated from A, B, C, and J must be reconciled.
4. The predicted lattice distortion must be less than $\sim 3\times 10^{-3}$.[5]

The values of $A=4$, $B=-6.5$, and $C=-16$ obtained from the point-charge calculation compare quite favorably with the values obtained from the fit. Furthermore, it is seen that the values obtained certainly give $B,C \gg A$ and $\delta \gg \eta$. In fact, A and η are almost negligibly small.

The value of η calculated from A is -2.5 cm^{-1}, closer to the fit value of -2.2 cm^{-1} than is reasonable to expect. In the regime where there is a close competition between the Jahn-Teller forces and the exchange energy $\sin 2\theta'$ is a very sensitive function of ϵ_1, ϵ_2, and ϵ_3. To reconcile the $\sin 2\theta'$ value, obtained from the fit, to that predicted from the values of A, B, and C given by the fit, we first compute $\epsilon_1=35$ cm^{-1}, $\epsilon_2=300$ cm^{-1}, and $\epsilon_3=1.4$ cm^{-1}. It is clear ϵ_3 can be neglected throughout. The ratio of ϵ_2/ϵ_1 required to give $\sin 2\theta'=0.375$ is 4.4. The actual ratio is 8.5. The agreement is quite satisfactory, considering the approximations used to derive the indirect quadrupole interaction in terms of A, B, and C.

It remains to predict the distortion induced by ordering. Substituting into Eq. (15) we have

$$|S_1|\sim|S_2|\sim 0.5\times 10^{-4}, \quad |S_3|\sim 1.\times 10^{-4},$$
$$S_4=S_5=0, \quad |S_6|\sim 3\times 10^{-4}.$$

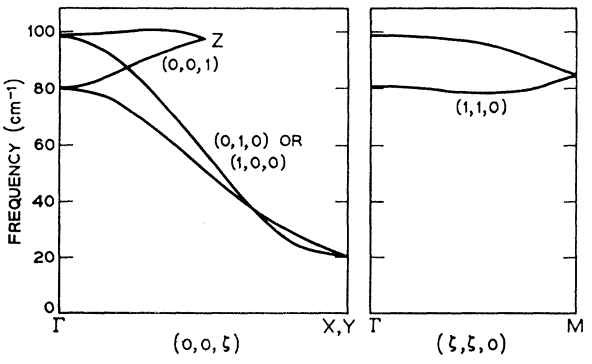

FIG. 9. Spin-wave dispersion predicted by the fit in text.

The surprisingly small value for S_6 is due to the cancellation of $B/\sqrt{3}$ by $(G/H)C$ in (16). This same term enters ϵ_2 and makes a negligible contribution to ϵ_2. The term that persists in the expression for ϵ_2 is the contribution from purely internal distortions (of the order of 10^{-2}) which, of course, do not appear in the expression for the strain. This explains why large anisotropies and lattice interactions do not lead to large external distortions in UO_2. This result would not be apparent in a phenomenological discussion of the magnetoelastic energy. The strains predicted are too small to have been seen by neutron scattering. There is no contradiction with the length change $\Delta l/l<10^{-4}$ measured by Brandt and Walker.[3] Length changes measured on a polydomain sample effectively measure a strain determined by averaging (15) over equivalent directions and will give results appreciably less than those predicted above.

IV. SUMMARY AND CONCLUSIONS

A satisfactory model for the ground-state and low-lying electronic excitations in the presence of strong spin-lattice coupling has been derived for antiferromagnetic UO_2. The local spin-lattice interaction is formulated in terms of the Jahn-Teller effect and parametrized by three constants. The interaction is used to derive the lattice-spin ground state and the spin-wave excitations in a consistent manner. The parameters obtained by fitting the spin-wave energies and wave functions to experiment are shown to be consistent with the ground-state calculation and are reasonable when compared to the predictions of a point-charge calculation.

We may conclude from our investigation that in a system like UO_2 with a large orbital ground-state degeneracy, the interaction with the lattice leads to indirect quadrupole-quadrupole pair interactions that are as strong as the exchange terms. The calculation of the ground state reveals a competition between cooperative Jahn-Teller forces and exchange energy that leads to a ground state with a less than fully polarized spin. The extension of these results to a calculation of the thermodynamic properties, in particular the order of the phase transition, will be discussed in a future publication.

ACKNOWLEDGMENTS

The author takes pleasure in acknowledging the many suggestions and valuable assistance provided by W. F. Brinkman. Interesting discussions were also had with J. Appelbaum and F. L. Varsanyi. He also wishes to thank R. Cowley and G. Dolling for providing a sample of UO_2 and their unpublished data. D. E. Hendrix of the Oak Ridge National Laboratory cooperated by providing floating-zone UO_2. The technical assistance of F. DeRosa in carrying out the far-infrared measurements is also appreciated.