

(4) There have been theories developed^{16,19} for the phonon thermal conductivity at magnetic phase transitions employing the coupling term (1). Since they also use the small- q approximation, these theories are in principle equivalent to the theory of ultrasonic attenuation. They, however, do not use the factorization procedure. They can express their result in terms of the specific heat C and the spin thermal conductivity κ . In this way the sound attenuation, or the reciprocal of the phonon relaxation time, becomes proportional to κ , all

other singular factors cancelling. A theory for κ at the magnetic phase transition has not been developed so far. Similar ideas have recently been expressed by Huber.²⁰

ACKNOWLEDGMENTS

Further experiments, studying other magnetic substances, are in progress. Informative discussions with Dr. Abrahams, Dr. Bennett, Dr. Huber, and Dr. Pytte are gratefully acknowledged.

¹⁹ K. Kawasaki, Progr. Theoret. Phys. (Kyoto) **29**, 801 (1963).

²⁰ D. L. Huber, Phys. Letters **25A**, 93 (1967).

Spin-Lattice Interaction in UO_2 . II. Theory of the First-Order Phase Transition

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A theory of the first-order phase transition in UO_2 is presented and discussed in the molecular-field approximation. An isotropic nearest-neighbor exchange and local quadrupole-lattice interaction are taken as the basic interactions in the model. Interesting behavior is obtained due to the two distinct ways in which the collective ground-state degeneracy can be removed at $T=0^\circ\text{K}$: a cooperative Jahn-Teller distortion or a polarization of the sublattice magnetization by the exchange field. Depending on the relative gain in free energy obtained by these two mechanisms, one obtains four different types of behavior near the critical point: (1) a second-order transition to a distorted state with no magnetic ordering; (2) a second-order transition to a distorted state followed by a second-order magnetic transition; (3) a first-order transition yielding a discontinuous change in lattice distortion and sublattice magnetization; (4) a second-order magnetic transition accompanied by a weak distortion. The temperature dependence of the elastic constant C_{44} is also derived. The parameters required to give a first-order transition in agreement with the measured discontinuity in sublattice magnetization and the correct behavior for C_{44} are found to be consistent with the parameters obtained from the measured spin-wave excitations.

I. INTRODUCTION

INTERACTION between the single-ion ground state and lattice is expected to be large in systems where the ground-state degeneracy is associated with the orbital state of the electrons. In a concentrated system both the collective ground state and low-lying electronic excitations will be significantly modified by this interaction. Uranium dioxide is a particularly striking example of this situation. In a previous paper,¹ (henceforth referred to as I), it has been shown that the ground state is characterized by a balance between the exchange and Jahn-Teller (JT) forces and that indirect quadrupole-quadrupole interactions caused by the virtual exchange of an optical phonon must be included to obtain the proper excitation spectra. Since

much of the current interest in UO_2 was stimulated by the observations of Frazer *et al.*² that the transition to the ordered state was a first-order phase transition and the subsequent explanations of Blume,³ it is particularly interesting to consider whether the spin-lattice interaction used to obtain the ground state and spin-wave excitations is able to generate the first-order phase transition.

In the following, the thermodynamic properties of UO_2 are derived in the molecular-field approximation. Interesting effects are obtained due to the two distinct ways in which the ground state degeneracy can be removed at $T=0^\circ\text{K}$ —a cooperative JT distortion or the usual polarization of the sublattice magnetization

² B. C. Frazer, G. Shirane, D. E. Cox, and C. E. Olsen, Phys. Rev. **140**, A1448 (1965).

³ M. Blume, Phys. Rev. **141**, 517 (1966).

¹ S. J. Allen, Jr., Phys. Rev. **166**, 530 (1968).

by the exchange field. In the regime where the gains in free energy due to these two mechanisms are comparable, interesting complications occur.

II. THEORY OF THE PHASE TRANSITION

In the molecular-field approximation the total Gibbs free energy is given by

$$G = -kT \ln Z + \frac{1}{2} z_u J \langle \mathbf{S} \rangle^2 + \frac{1}{2} \sum_{k\alpha} \sum_{k'\beta} \left\{ \begin{matrix} k & k' \\ \alpha & \beta \end{matrix} \right\} u_\alpha(k) u_\beta(k') + \sum_{k\alpha} \sum_{\rho} \left\{ \begin{matrix} k \\ \alpha \end{matrix} \right\} u_\alpha(k) U_\rho + \frac{1}{2} \sum_{\rho\sigma} \{\rho\sigma\} U_\rho U_\sigma, \quad (1)$$

where $z_u (=4)$ is the effective number of uranium spins contributing to the exchange field and J is the exchange constant. $u_\alpha(k)$ is the internal displacement of the k th oxygen in the paramagnetic unit cell in the α th direction from the uranium ion and U_ρ is the external strain in the Voigt notation.⁴ For instance, $U_1 = U_{xx}$ and $U_4 = U_{yz} + U_{zy}$.

Z is the partition function given by

$$Z = \sum_{i=1}^3 \exp(-E_i/kT), \quad (2)$$

in which the E_i are the molecular-field energy levels. The spin Hamiltonian used to find the energy levels, used in the partition function, is the following.

$$H = -z_u J \langle \mathbf{S} \rangle \cdot \mathbf{S} - z_0 (Fr_0) \left\{ \left(\frac{A}{\sqrt{3}} \right) \left[\frac{1}{2} O_\theta (2U_3 - U_1 - U_2) + \frac{3}{2} O_\epsilon (U_1 - U_2) \right] + \left(\frac{B}{\sqrt{3}} \right) [O_{yz} U_4 + O_{xz} U_5 + O_{xy} U_6] + \frac{1}{2} C [O_{yz} (u_x(1) - u_x(2))/r_0 + O_{xz} (u_y(1) - u_y(2))/r_0 + O_{xy} (u_z(1) - u_z(2))/r_0] \right\}, \quad (3)$$

where $z_0 (=8)$ is the number of oxygen ions surrounding a uranium ion, r_0 is the uranium-oxygen separation $\approx 2.36 \text{ \AA}$, and F is a constant with the dimensions of force and given by

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

in which ze is the oxygen ionic charge, $\langle r_e^2 \rangle$ is the average $5f^2$ electron radius squared, and $\langle \alpha || J || \alpha \rangle$ is a reduced matrix element evaluated by Elliot and Stevens.⁵ In (3) the operators O are quadrupole or quadratic spin operators which operate on the effective $S=1$ ground-state manifold of the U^{4+} ion.^{6,7} They are

⁴ H. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), pp. 129 ff.

⁵ R. J. Elliot and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

⁶ C. A. Hutchinson, Jr., and G. A. Candela, J. Chem. Phys. **27**, 707 (1957).

⁷ H. U. Rahman and W. A. Runciman, J. Phys. Chem. Solids **27**, 1833 (1966).

as follows:

$$O_\theta = 3S_z^2 - S(S+1), \quad O_\epsilon = S_x^2 - S_y^2, \\ O_{\alpha\beta} = \frac{1}{2} (S_\alpha S_\beta + S_\beta S_\alpha). \quad (5)$$

The constants A , B , and C are left as adjustable parameters, and can be determined by including the spin-lattice interaction in a theory for the low-lying excitations and comparing with experiment, as was done in I. Likewise, in this discussion, they are left as parameters and are determined where they can be by fitting theory with experiments regarding the phase transition. Before proceeding it should be pointed out that the spin-lattice part of (2) is simply an expression of the JT effect in a concentrated salt assuming a homogeneous deformation.

To find the equilibrium magnetization and lattice distortion, one minimizes the Gibbs free energy, at fixed temperature T , with respect to the independent variables $\langle \mathbf{S} \rangle$, $\{u_\alpha(k)\}$, and $\{U_\rho\}$. The following relations are obtained:

$$0 = -z_u J \langle \mathbf{S} \rangle_T + z_u J \langle \mathbf{S} \rangle, \\ 0 = -z_0 (Fr_0) (A/\sqrt{3}) \langle O_\theta \rangle_T + \sum_{\sigma=1}^3 C_{3\sigma} U_\sigma, \\ 0 = +z_0 Fr_0 \frac{A}{2\sqrt{3}} \langle O_\theta \rangle_T - z_0 r_0 F \frac{3A}{2\sqrt{3}} \langle O_\epsilon \rangle_T + \sum_{\sigma=1}^3 C_{1\sigma} U_\sigma, \\ 0 = +z_0 Fr_0 \frac{A}{2\sqrt{3}} \langle O_\theta \rangle_T + z_0 r_0 F \frac{3A}{2\sqrt{3}} \langle O_\epsilon \rangle_T + \sum_{\sigma=1}^3 C_{2\sigma} U_\sigma, \\ 0 = -z_0 Fr_0 \frac{B}{\sqrt{3}} \langle O_{yz} \rangle_T + \frac{e^2}{4\pi\epsilon_0\Omega_0} r_0 G u_x(-) + \{44\} U_4, \\ \dots \\ 0 = -z_0 Fr_0 \frac{C}{2} \langle O_{yz} \rangle_T + \frac{e^2}{4\pi\epsilon_0\Omega_0} r_0 G U_4 \\ + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0\Omega_0} H u_x(-), \\ \dots$$

$$u_x(+) = u_y(+) = u_z(+) = 0, \quad (6)$$

where advantage has been taken of a simple transformation on the internal distortions

$$u_\alpha(+) = u_\alpha(1) + u_\alpha(2), \\ u_\alpha(-) = u_\alpha(1) - u_\alpha(2), \quad (7)$$

and where G and H , defined in I, are determined from the short-range force constants⁸ and Coulomb inter-

⁸ G. Dolling, R. A. Cowley, and A. D. B. Woods, Can. J. Phys. **43**, 1397 (1965).

actions⁹ between ions. C_{ij} are the elastic constants in the absence of spin-lattice interaction.⁴

The above conditions consist of a set of relations between the thermal average quadrupole moments and the strains, in addition to the usual requirement of self-consistency on the sublattice magnetization. Note that $\langle \mathbf{S} \rangle_T$ is the thermal average spin given by

$$\langle \mathbf{S} \rangle_T = Z^{-1} \sum_{i=1}^3 \langle i | \mathbf{S} | i \rangle \exp(-E_i/kT). \quad (8)$$

It is not the same as $\langle \mathbf{S} \rangle$, one of the molecular-field order parameters. However, to minimize the Gibbs free energy, $\langle \mathbf{S} \rangle_T = \langle \mathbf{S} \rangle$.

With the aid of (5) the problem can be simplified by using the average quadrupole moment as the independent variable. Since every set of quadrupole moments generates a unique set of external and internal strains, the free energy can be re-expressed in terms of the sublattice magnetization and local-quadrupole moment. The problem is further simplified by noting that the results of the ground state and spin-wave calculation indicate that A is much less than B or C . That is to say, the strong interaction occurs with the shear distortions rather than the compressional distortions. This is also apparent from the behavior of the elastic constants.¹⁰ In the following the compressional distortions are ignored entirely and we set $A = 0$. Assuming the configuration at $T = 0^\circ\text{K}$ consists of spins along a given $[110]$ direction, the free energy may be expressed in terms of only three variables; temperature, $\langle S_z \rangle$, the average spin in the $[110]$ direction, and $\langle O_{xy} \rangle$, the average quadrupole moment.

The free energy $G(\langle S_z \rangle, \langle O_{xy} \rangle, T)$ is given as

$$G = -kT \ln Z + \frac{1}{2} z_u J \langle S_z \rangle^2 + \frac{1}{2} (8\epsilon) \langle O_{xy} \rangle^2, \quad (9)$$

where the energy levels for Z are found from the following Hamiltonian:

$$-z_u J \langle S_z \rangle S_z - 8\epsilon \langle O_{xy} \rangle O_{xy}, \quad (10)$$

where

$$8\epsilon = \frac{1}{2} (4\pi\epsilon_0\Omega_0/e^2r_0^2) (C^2/H) (z_0Fr_0)^2 + (1/C_{44}) \frac{1}{3} (z_0Fr_0)^2 (B - \sqrt{3}C(G/H))^2. \quad (11)$$

(Note that $8\epsilon = \epsilon_2$ defined in I.)

At a given temperature T , the equilibrium values of $\langle S_z \rangle$ and $\langle O_{xy} \rangle$ are determined by finding the position in the $\langle S_z \rangle, \langle O_{xy} \rangle$ plane, within the region $0 \leq \langle S_z \rangle \leq 1$ and $0 \leq \langle O_{xy} \rangle \leq \frac{1}{2}$, that gives an absolute minimum for G , the Gibbs free energy in (9). In this manner we determine $\langle S_z \rangle$ and $\langle O_{xy} \rangle$ as a function of temperature, and the position and character of the transition points. The nature of the phase transition is determined by the

relative size of the magnetoelastic energy ϵ and the exchange energy $z_u J$. Four distinct types of phase transition may be obtained depending on the ratio

$$f = \epsilon/z_u J.$$

(1) $f > 1$. There is no magnetic ordering at any temperature. At $T = (4/3)(\epsilon/k)$ a second-order transition to a cooperative JT distorted state is obtained.

(2) $1 \geq f \geq \frac{1}{2}$. Two transitions occur. As the temperature is lowered one first encounters a second-order transition to a JT distorted state followed by a second-order magnetic transition.

(3) $\frac{1}{2} \geq f \geq 2/7$. The transition is a first-order transition, generating discontinuously a local magnetization and quadrupole moment.

(4) $2/7 \geq f \geq 0$. The quadrupole moment or lattice distortion and sublattice magnetization appear simultaneously, but they suffer no discontinuity. The transition temperature is independent of f in this region and equal to $\frac{2}{3}z_u J/k$.

In Fig. 1, the results are summarized by plotting transition temperature normalized to the exchange energy $z_u J$ against normalized magnetoelastic energy f . The curves generated separate the three regions where one has either a paramagnetic, nondistorted state, a distorted state without a sublattice magnetic moment or both a magnetically ordered and distorted state. A purely magnetically ordered state cannot occur, for it is easily shown that the presence of an average local magnetization necessitates an average-quadrupole moment. The converse is not true.

In Fig. 2 is plotted the discontinuity in $\langle S_z \rangle$ and $\langle O_{xy} \rangle$ at the transition as a function of f . Also shown is $\Delta \langle S_z \rangle / \langle S_z \rangle_{T=0^\circ\text{K}}$. The largest value of $\Delta \langle S_z \rangle / \langle S_z \rangle_{T=0^\circ\text{K}}$ that can be obtained is just slightly greater than 0.5. If we assume a value of 0.5, corresponding to the observations of Frazer *et al.*,² one obtains a value of $f \approx 0.450$. Sublattice magnetization versus temperature

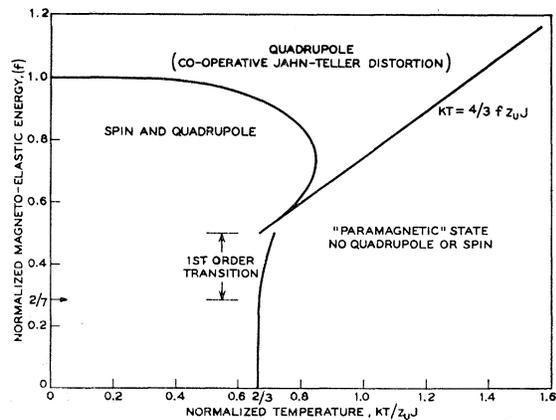


Fig. 1. Transition temperature versus normalized magnetoelastic energy f .

⁹ R. Srinivasan, Proc. Phys. Soc. (London) **72**, 566 (1958).
¹⁰ O. G. Brandt and C. T. Walker, Phys. Rev. Letters **18**, 11 (1967).

for $f=0.450$ is compared with experiment in Fig. 3. It is clear that the theory is capable of producing the discontinuity but falls far short of a good detailed fit. The transition occurs at $kT=0.7z_uJ$. From the neutron² work, $T_N=30.8^\circ\text{K}$, which gives $z_uJ=44^\circ\text{K}$ or 32.4 cm^{-1} . The latent heat is found to be $\sim 2\text{ J/cm}^3$.

III. SUSCEPTIBILITY AND ELASTIC CONSTANTS ABOVE T_N

Above the transition, expansion of the free energy in $\langle S_z \rangle$ and $\langle O_{xy} \rangle$ about $\langle S_z \rangle=0$ and $\langle O_{xy} \rangle=0$ is valid. The terms that are present are

$$G = \alpha \langle S_z \rangle^2 + \beta \langle O_{xy} \rangle^2 + \gamma \langle S_z \rangle \langle O_{xy} \rangle + \delta \langle O_{xy} \rangle^3 + \dots \quad (12)$$

Since there are no $\langle S_z \rangle \langle O_{xy} \rangle$ terms, there will be no linear magnetostrictive effect and the high-temperature susceptibility will be unchanged from that obtained in absence of spin-lattice coupling. Experimentally from 40 to 300°K the susceptibility can be fit to a Curie-Weiss law with a θ value equal to $\sim 200^\circ\text{K}$.¹¹ The simple model used in the phase-transition calculation gives $\theta=2z_uJ=88^\circ\text{K}$. The deviation is too large to be ignored. A molecular-field treatment of the high-temperature susceptibility is expected to be better than a molecular-field treatment of the transition temperature. That is to say, the value of z_uJ inferred from the transition temperature is suspect. It should also be noted that the inclusion of other than nearest-neighbor exchange will alter θ but probably not sufficiently to make up the present deficit.

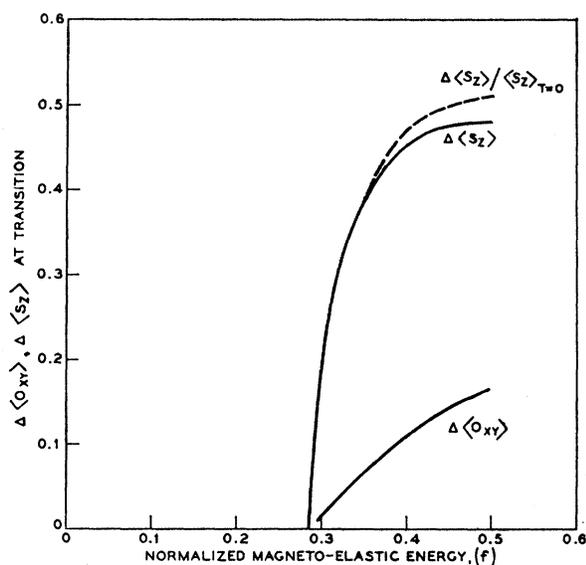


FIG. 2. Discontinuity in $\langle S_z \rangle$ and $\langle O_{xy} \rangle$ as a function of f in the region of the first-order transition.

¹¹ M. J. M. Leask, L. E. J. Roberts, A. J. Walter, and W. P. Wolf, *J. Chem. Soc.* **1963**, 4788 (1963).

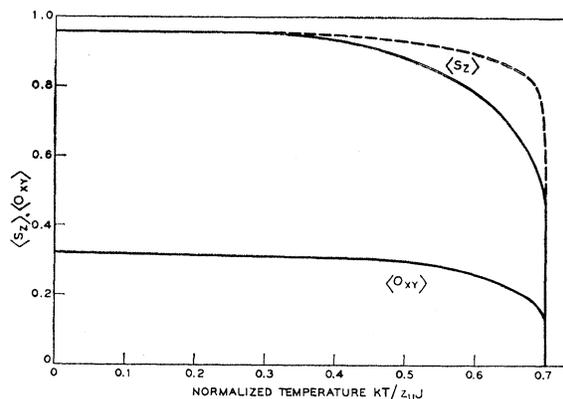


FIG. 3. Sublattice magnetization and quadrupole moment versus temperature for $f=0.450$. The dashed curve is the experimental result of Frazer *et al.* (Ref. 2).

The elastic constant C_{44} in the paramagnetic region may be calculated from Eq. (1). Since the lattice distortion produces no sublattice magnetization the exchange energy in Eq. (1) may be ignored. The thermal part of the free energy, $-kT \ln Z$, is expanded to second order in the internal strain $u_z(-)/r_0$, and external strain U_4 .

$$-kT \ln Z = -kT \ln 3 - \frac{1}{12} (\lambda^2/kT), \quad (13)$$

where

$$\lambda = Fr_0 \left[\frac{1}{3} \sqrt{3} (z_0 B) U_4 + \frac{1}{2} (z_0 C) u_z(-)/r_0 \right]. \quad (14)$$

The free energy is now in quadratic form and expressed in terms of the internal and external strains.

$$G = -kT \ln 3 - \frac{1}{12} \frac{(Fr_0)^2}{kT} \left[\frac{z_0 B}{\sqrt{3}} U_4 + \frac{1}{2} (z_0 C) (u_z(-)/r_0) \right]^2 + \frac{1}{2} \left(\frac{1}{2} \frac{e^2}{4\pi\epsilon_0\Omega_0} H \right) u_z(-)^2 + \frac{e^2}{4\pi\epsilon_0\Omega_0} G r_0 u_z(-) U_4 + \frac{1}{2} \{4, 4\} U_4^2. \quad (15)$$

The elastic constant $C_{44}(T)$ is obtained from (15) by calculating

$$d^2G/dU_4^2 = C_{44}(T). \quad (16)$$

It must be noted that the internal strain $u_z(-)/r_0$ is not an independent variable and adjusts itself for a given external strain U_4 , to minimize the energy in (15).⁴

Performing the necessary manipulations one obtains

$$C_{44}(T) = C_{44}(\infty) \left[\frac{(T - T_i - T_e)}{(T - T_i)} \right], \quad (17)$$

where $C_{44}(\infty)$ is the elastic constant in the absence of spin-lattice coupling or at arbitrarily high temperatures. $C_{44}(\infty)$ is itself a temperature-dependent quantity but over the temperature range of interest, from T_N to room temperature, the variation should be at most a few percent and we ignore this complication. The tem-

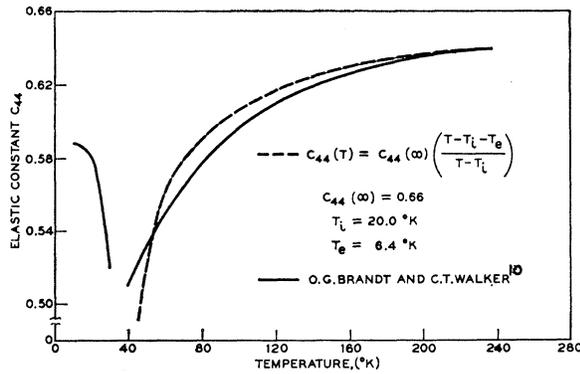


FIG. 4. Elastic constant C_{44} versus temperature.

peratures T_i and T_e are defined as

$$T_i + T_e = \frac{4}{3}\epsilon/k, \quad (18)$$

that is to say, the temperature at which one would have a second-order cooperative JT distortion in the absence of any exchange interaction, and

$$T_i = \frac{1}{12}(4\pi\epsilon_0\Omega_0/e^2r_0^3)(C^2/H)(z_0Fr_0)^2. \quad (19)$$

T_i is the temperature at which a purely internal instability would occur if the coupling to the external distortion should disappear. Under that rather singular condition, $T_e = 0^\circ\text{K}$, there would be a lattice instability but it would not manifest itself by a softening of the elastic constant C_{44} .

In Fig. 4 the high-temperature behavior of the elastic constant C_{44} is compared with experiment. The theoretical curve is fixed to experiment at $T = 240^\circ\text{K}$. $T_i + T_e$ is taken as 26.4°K , the value given by $f = 0.450$ and $z_u J = 44^\circ\text{K}$. T_e is taken to be 6.4°K , $C_{44}(\infty) = 0.66$. Although Eq. (13) fails to give a detailed fit, it clearly displays the experimental features in a semiquantitative manner.

IV. DISCUSSION

A comparison of parameters used to describe the phase transition and elastic constant anomaly with those used to obtain the proper spin-wave excitations can be made. It is clear that the theory is not sufficient to extract precise values for the interaction constants but good estimates can be extracted from the semiquantitative fit. From the present discussion we have

$$z_u J = 32.4 \text{ cm}^{-1},$$

$$|A| = \text{assumed } 0,$$

$$|B| = \text{undetermined},$$

$$|C| = 16.2,$$

$$|B - (G\sqrt{3}/H)C| = |B - 1.03C| = 4.4;$$

from these values we infer that the ground-state spin deviation is

$$(S_z - \langle S_z \rangle) / S_z = 0.043$$

and that the external and internal distortions are

$$U_1 = U_2 = U_3 = U_4 = U_5 = 0,$$

$$|U_6| \cong 3 \times 10^{-3},$$

$$|u_z(-)/r_0| \cong 4 \times 10^{-3}.$$

In comparison, the spin-wave calculation gave

$$z_u J = 35.0 \text{ cm}^{-1},$$

$$|A| = 1.5,$$

$$|B| = 31.5,$$

$$|C| = 31,$$

$$|B - 1.03C| = 0.4,$$

from which values one has for the spin deviation

$$(S_z - \langle S_z \rangle) / S_z = 0.063$$

and for the strains

$$|U_1| = |U_2| \cong 0.5 \times 10^{-4}, \quad |U_3| \cong 10^{-4},$$

$$|U_4| = |U_5| = 0, \quad |U_6| \cong 3 \times 10^{-4},$$

$$|u_z(-)/r_0| \cong 8 \times 10^{-3}.$$

The only serious discrepancy occurs with regard to $|B - (G\sqrt{3}/H)C|$. The nearly complete cancellation obtained with the values of B and C calculated from the spin waves must be regarded as somewhat artificial. Certainly, $G\sqrt{3}/H$ obtained from the force constants cannot be known to within better than $\sim 15\%$, which would allow a value for $|B - (G\sqrt{3}/H)C|$ as large as that obtained by fitting to the elastic-constant behavior. However, we still conclude that strongest interaction occurs between the quadrupole and the internal distortions.

Although the effect of the quadrupole-lattice interaction in UO_2 is treated throughout in the simplest approximation, the theory describes the experimental situation sufficiently well to make meaningful estimates of the relevant parameters. At the same time, three important consequences of the non-Kramers, orbital ground-state degeneracy are revealed.

(1) At $T = 0^\circ\text{K}$ competition between JT forces and exchange energy cause the spin to be reduced from its fully polarized state. (2) The spin-wave excitations from the ground state are significantly modified by quadrupole-quadrupole interactions produced by the virtual exchange of an optical phonon. (3) Since the collective ground-state degeneracy can be lifted by a cooperative JT distortion as well as an exchange field, the properties of the system at the critical point become complicated and may exhibit multiple transitions, a first-order transition, or no magnetic ordering at all.

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