Theory of the First-Order Magnetic Phase Change in UO_2^{\dagger}

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A simple model accounts semiquantitatively for the first-order magnetic phase change observed recently in UO_2 by Frazer, Shirane, Cox, and Olsen. The model assumes that the electronic structure of the paramagnetic U4+ ion consists of a nonmagnetic singlet ground state and a low-lying magnetic triplet, and that only bilinear isotropic exchange interactions are present. In a molecular-field theory the triplet is split by an internal field proportional to the magnetization. If the molecular field is sufficiently strong, one of the components of the triplet will lie, in the magnetic state, below the singlet, and a self-consistent magnetic solution is obtained at T=0. Increasing the temperature causes the magnetization to be reduced, and the low-lying component of the triplet is raised in energy. It is shown that a "catastrophe" may occur at some critical temperature so that the magnetization is reduced discontinuously to zero. It is also found that, depending on the ratio of the singlet-triplet energy difference to the molecular-field splitting of the triplet, one obtains either no magnetic ordering, a first-order phase change, or a second-order transition.

I. INTRODUCTION

 $\mathbf{R}^{ ext{ECENTLY, Frazer, Shirane, Cox, and Olsen¹ have shown that the paramagnetic-antiferromagnetic}$ transition which occurs in UO₂ at about 30°K is a firstorder phase change. The transition is unaccompanied by any discernible change in the lattice volume or structure, indicating that the order of the phase change is inherently a consequence of the magnetic properties of the system.

First-order magnetic phase changes have been considered by a number of authors in recent years. Bean and Rodbell² pointed out that a magneto-mechanical coupling could cause what would otherwise be the usual second-order magnetic phase transition to become a first-order transition with the associated discontinuous change in the magnetization at the transition temperature. This theory predicts that a change in the crystal volume should accompany the magnetic phase change, so that it does not appear to be applicable to the case of UO₂. Later, Rodbell, Jacobs, Owen, and Harris³ showed that the presence of biquadratic exchange in the magnetic Hamiltonian could cause the temperature dependence of the magnetization to become increasingly steep near the Curie point and in some circumstances to become discontinuous there. The magnetic properties of MnO were interpreted by these authors as requiring the presence of biquadratic exchange. Lines and Jones^{4,5} have recently questioned this interpretation, and they suggest that the behavior of MnO can be understood solely on the basis of bilinear exchange. The magnitude of the biquadratic exchange integral is extremely difficult to estimate theoretically, and the applicability

of this to the explanation of the properties of UO_2 is not clear.

In this paper it is shown that a first-order magnetic phase transition can occur solely in the presence of isotropic bilinear exchange and of crystal-field splittings of the proper magnitude and sign. It is shown that it is plausible that the appropriate crystal-field effects should occur in UO₂. Good qualitative agreement is obtained with the work of Frazer et al. on the basis of a simple molecular-field calculation.

The proposed model can be discussed quite simply with reference to Fig. 1. We assume that the electronic ground state of the magnetic ion is a singlet, and that a triplet level lies at an energy Δ above the singlet. The magnetic properties of such ions are well known-they are the subject of a problem in Kittel's book.⁶ In a magnetic field the triplet level is split, while the singlet remains unaffected. If the magnetic field is sufficiently large, as in Fig. 1(b), the lowest state will be one of the magnetic components of the triplet, rather than the nonmagnetic singlet. At $T=0^{\circ}$ K, all of the ions will be in this ground state and the system will have a net magnetic moment. If the magnetic field is smaller than $\Delta/g\mu_{\rm B}$, however, the energy level diagram is as in Fig. 1(a), and the system is nonmagnetic at $T=0^{\circ}$ K. Suppose now that the magnetic field is due to exchange interactions between the various ions. On the basis of a molecular-field approximation, the field is then given by λM , where λ is a constant whose magnitude depends on the size of the exchange integral. If λ is sufficiently large, the energy level diagram at low temperatures will be as in 1(b). At absolute zero the magnetization is then indeed saturated, as it must be in order to produce the energy level diagram shown, so that a self-consistent solution for M is obtained. A level scheme such as the one in Fig. 1(a) is not, however, possible (if the magnetic field is internal) at $T=0^{\circ}$ K, since the splitting of the triplet requires a nonzero net magnetization, but all of the ions are in the singlet state, so that no non-

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¹B. C. Frazer, G. Shirane, D. E. Cox, and C. E. Olsen, Phys. Rev. 140, A1448 (1965). A similar study has also been done by B. T. Willis and R. I. Taylor, Phys. Letters 17, 188 (1965).
² C. P. Bean and D. S. Rodbell, Phys. Rev. 126, 104 (1962).
³ D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, Phys. Rev. Letters 11, 10 (1963).
⁴ M. E. Lines and E. D. Jones, Phys. Rev. 139, A1313 (1965).

⁵ M. E. Lines (private communication).

⁶ C. Kittel, Introduction to Solid State Physics (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 232.



FIG. 1. Energy-level diagram (a) for magnetic-field splitting smaller than the singlet-triplet separation Δ , and (b) for magneticfield splitting larger than $\dot{\Delta}$.

zero self-consistent solution for the magnetization can be found. The self-consistency condition requires that the triplet be unsplit in this case. If the system is to be magnetic, then, it is necessary that the exchange splitting of the triplet be at least larger than the crystalfield splitting Δ at T=0. The temperature dependence of the magnetization can then be followed by noticing that an increase of the temperature leads to a population of the excited states in Fig. 1(b), including the nonmagnetic singlet. This in turn leads to a decrease of the magnetization, which in turn leads to a decrease in the splitting of the triplet. At each temperature the magnetization is determined self-consistently by these effects.

A first-order phase transition can arise in these circumstances if a slight increase in temperature leads to a substantial increase in the population of the nonmagnetic singlet. The resulting reduction in the splitting of the triplet could then lead to a "catastrophe" in which a nonzero self-consistent solution is no longer possible, or to a situation in which the free energy of the unmagnetized state is lower than the free energy of the magnetized state of the solid. This would involve a discontinuous jump in the magnetization, i.e., a firstorder transition. That this does in fact occur is shown in the following sections.

The model proposed here for UO_2 is superficially similar to that proposed for europium metal by Bozorth and Van Vleck,⁷ and to several "induced moment" systems treated by Bleaney,⁸ Trammell,⁹ and Grover.¹⁰ In the europium case there is indeed a nonmagnetic singlet (J=0) level lying below a triplet (J=1) level. The exchange interaction is not large enough to cause a crossing of the singlet and one of the triplet states, however, and the magnetization is supposed due to the induction by the exchange interaction of a moment in the singlet. This proceeds via off-diagonal matrix elements of the exchange interaction between the J=0and J=1 states, similar to the well-known Van Vleck

141

temperature-independent paramagnetism, which is induced by an external field rather than by the exchange interaction. In the UO₂ case we do not consider that the Van Vleck mechanism plays a major role in the magnetization curve, although it may play a small part in the size of the saturation moment. As will be seen, there are no off-diagonal elements of exchange between the singlet and the triplet, so that the singlet in UO₂ plays a relatively inert role. Its major contribution to the magnetization curve comes about simply by its being occupied, and this is sufficient to change the magnetic transition to first order.

II. ELECTRIC STRUCTURE OF UO₂

The form-factor measurements of Frazer et al. show that the electronic configuration of U^{4+} in UO_2 is $(5f)^2$. The Hund's rule ground state, assuming Russell-Saunders (LS) coupling is ${}^{3}H_{J=4}$. In the actinide series it is well known that serious departures from LS coupling are found, but we may still expect that the ground state will be a J=4 level, even in the presence of intermediate coupling. UO₂ crystallizes in the CaF₂ structure, so that the U4+ ions fall on a face-centered cubic lattice, and each of the ions in the center of a cube, with eight O²⁻ ions at the corners. The effect of the crystal field of such an array of ions on the $(5f)^2$ configuration has been considered by Hutchison and Candela¹¹ and by Lea, Leask, and Wolf.¹² The J = 4 level is split in a cubic environment into a singlet (Γ_1) , a doublet (Γ_3), and two triplets (Γ_4, Γ_5). Point-charge calculation shows that in the cubal environment of UO_2 , the U⁴⁺ ground state is either Γ_1 or Γ_5 , and that the factor which determines the lower of these levels is the ratio of fourth-order to sixth-order cubic crystal-field parameters. There is no point in estimating this ratio with a point-charge model since the reliability of such calculations is small for such relatively delicate considerations. We will assume here that the Γ_1 singlet lies below the Γ_5 triplet by an energy Δ , and show that this plausible arrangement explains the results of Frazer et al. The energy levels are then as shown in Fig. 2. The magnetization process for UO_2 will then be as described in the Introduction, with the exchange interaction



¹¹ C. A. Hutchison and G. A. Candela, J. Chem. Phys. 27, 707

⁷ R. M. Bozorth and J. H. Van Vleck, Phys. Rev. 118, 1493 (1960).

⁸ B. Bleaney, Proc. Roy. Soc. (London) **A276**, 19 (1963). ⁹ G. T. Trammell, Phys. Rev. **131**, 932 (1963).

¹⁰ B. Grover (to be published).

^{(1957).} ¹² K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).

causing a splitting of the Γ_5 level, so that one of its components lies below the Γ_1 level in the magnetized state. If LS coupling is assumed, the magnetic moment of the Γ_5 level is calculated to be 2 Bohr magnetons. This is quite close to the observed saturation magnetization of $1.8\mu_{\rm B}$,¹ and it suggests that the Γ_5 level is somehow involved in the magnetism of the U^{4+} ion. It should be noted that, although $2\mu_{\rm B}$ is the "spin-only" value of the magnetic moment, the explanation proposed here is not based on quenching of the orbital magnetic moment, since the crystalline field has been assumed smaller than spin-orbit coupling. The Γ_5 level arises from the 3H_4 ionic state, and its magnetic moment is predominantly orbital. There are three possible causes for the discrepancy between theory and experiment of $0.2\mu_{\rm B}$. These are (i) breakdown of LS coupling, (ii) off-diagonal crystal-field matrix elements, and (iii) off-diagonal matrix elements of the exchange interaction. The effect of (i) is easily shown to be to increase the moment of $2\mu_{\rm B}$ of the Γ_5 level. This is because the other J=4 levels $({}^{1}I_{4} \text{ and } {}^{1}G_{4})$ which would be mixed into the ${}^{3}H_{4}$ level by spin-orbit coupling have larger Landé g values than the ${}^{3}H_{4}$ level. The effect of (ii) could go in either direction. Here the crystalline field mixes into the Γ_5 level a component which arises from a different J level. Accurate calculation of this effect requires a knowledge of the effects of (i), since these influence the energy denominators in the perturbation calculation. It is quite reasonable that a combination of (i) and (ii) should account for the $0.2\mu_{\rm B}$. The effects of (iii) are rather more interesting than are those of (i) and (ii), since they can conceivably influence the statistical mechanics of the transition as well as the size of the saturation moment. The exchange interaction transforms as Γ_4 with respect to a single ion, since it is a vector interaction. There are therefore no matrix elements of exchange between the Γ_1 and Γ_5 levels, so the situation in UO₂ is quite different from that found by Bozorth and Van Vleck in Eu metal. We do not expect, then, that an appreciable moment will be induced in the Γ_1 level by this mechanism. There are matrix elements, however, between the Γ_1 level and the excited Γ_4 level, as well as between Γ_4 and Γ_5 . These matrix elements will induce a small moment in the Γ_1 and Γ_5 levels, but this should have little effect on the statistical mechanics of the phase transition, since it should be small compared to the inherent moment of the Γ_5 level. It can, however, make a contribution to the difference between the observed moment and the $2\mu_{\rm B}$ of the Γ_5 level. This contribution will be proportional to the sublattice magnetization itself, and so it is effective only in the antiferromagnetic region. It will therefore give rise to a difference in the magnetic moment as observed in the paramagnetic and antiferromagnetic states. The calculation of the effects of (i), (ii), and (iii) requires detailed knowledge of a number of parameters, such as the spin-orbit coupling constant, the fourth- and sixth-order cubic-field constants, Coulomb integrals (to estimate the energy of excited mul-

tiplets), and exchange integrals. It does not appear to be worthwhile to attempt such a calculation with the limited data available for the fixing of these parameters. Accordingly, only the simple system consisting of the Γ_1 and Γ_5 levels separated by energy Δ will be treated.

III. MOLECULAR-FIELD THEORY OF THE TRANSITION

The partition function for a system having an energylevel structure as in Fig. 1 in external magnetic field is

$$Z = 1 + e^{-\Delta/kT} (1 + e^{g\mu_{\rm B}H/kT} + e^{-g\mu_{\rm B}H/kT}), \qquad (1)$$

where g is the g factor of the excited triplet, $\mu_{\rm B}$ is the Bohr magneton, and H is the external magnetic field. The magnetic moment M is given by

$$M = \left(\frac{\partial F}{\partial H}\right)_{T} = -kT \frac{\partial}{\partial H} \ln Z,$$

$$= g\mu_{\rm B} \frac{e^{g\mu_{\rm B}H/kT} - e^{-g\mu_{\rm B}H/kT}}{e^{\Delta/kT} + 1 + e^{g\mu_{\rm B}H/kT} + e^{-g\mu_{\rm B}H/kT}}.$$
 (2)

This reduces to the familiar Brillouin function for spin 1 if the term $e^{\Delta/kT}$ in the denominator is ignored. Indeed, if $\Delta \rightarrow -\infty$, so that the singlet level lies well above the triplet, the Brillouin function is recovered. For positive Δ (singlet lowest) and for small magnetic field, the magnetization is zero at $T=0^{\circ}$ K, rises to a maximum, and then falls off according to a Curie-Weiss law, $M \propto H/(T+\Delta/4k)$.

We now need to calculate the magnetization when the magnetic field is an "internal" field, resulting from exchange interactions between the ions. In the molecular-field approximation for a ferromagnet in the absence of an external field, we have $H = \lambda M$, where λ is a constant which depends on the exchange integral. The equations for the magnetization then become

$$M = g\mu_{\rm B}(e^x - e^{-x}) / (e^{\Delta/kT} + 1 + e^x + e^{-x}), \qquad (3a)$$

$$x = g\mu_{\rm B}\lambda M/kT; \quad M = kTx/g\mu_{\rm B}\lambda.$$
 (3b)

The familiar graphical solution of these equations is not as easy here as for the simple case of a spin-1 ion. This is due to the term $e^{\Delta/kT}$ in the denominator of (3a). In the simple case $(\Delta \rightarrow -\infty)$ the solution is obtained by plotting M as a function of x according to Eq. (3a), and looking for the point of intersection of this curve with the straight line of Eq. (3b). Changing the temperature then simply causes a change in the slope of (3b), as in shown in Fig. 3. The Curie temperature is then determined by the condition that the slope of the straight line be equal to the slope of the other curve at the origin. If Δ is finite, however, this graphical method of solution is complicated by the fact that a change in temperature causes not only a change in the slope of the straight line (3b), but a change in the curve (3a) as well. This can be remedied by substituting (3b) for kT in (3a), so that (3a) becomes

$$M = g\mu_{\rm B}(e^x - e^{-x}) / (x\Delta/e^{g\mu_{\rm B}\lambda M} + 1 + e^x + e^{-x}). \quad (3a')$$

This is now an equation for M which must be solved graphically itself before the usual graphical procedure for the determination of M as a function of T is empolyed. Rewriting (3a') in dimensionless units by defining $M' = M/g\mu_{\rm B}$ and $\Delta' = \Delta/(g\mu_{\rm B})^2\lambda$, we have

$$M' = (e^{x} - e^{-x})/(e^{x\Delta'/M'} + 1 + e^{x} + e^{-x}). \quad (3a'')$$

M'=0 is always a solution of this equation for $\Delta'>0$. In the limit of large x, we have $M' \sim 1/[e^{x(\Delta'/M'-1)}+1]$ so that M'=1 is a solution of $\Delta' < 1$, but for $\Delta' > 1$ only the solution M'=0 exists. Hence there is no ordered state for $\Delta' > 1$. This is physically quite reasonable since for $\Delta' > 1$ the energy-level diagram for the magnetically saturated system is as in Fig. 1(a), i.e., the exchange is not strong enough to overcome the crystal-field splitting Δ . For $0.4 < \Delta' < 1.0$ the solutions of (3a'') are as shown in Fig. 4. At any temperature the intersection of the straight line of Eq. (3b) gives either three solutions for M', or only one (M'=0 is always a solution). It is found in the following that one of the three solutions maximizes the free energy while the other two give minima. It is clear that there will be a discontinuous jump in the magnetization from a finite value to zero at a critical temperature, so that the phase transition is of the first order. For $0.3662 < \Delta' < 0.4$ the solutions are as in Fig. 5. Here there are ranges of temperature for which there are (a) two solutions, (b) three solutions, and (c) one solution for M' as a function of T. The phase change is again of the first order, as there is a discontinuous jump in the magnetization at the critical temperature. For $\Delta' < 0.3662$ the situation is similar to the simple case shown in Fig. 3, and the phase change is of the second order, in that the magnetization goes uniformly to zero as the temperature is increased.

To discuss the stability of the various solutions it is necessary to calculate the Gibbs free energy as a func-



FIG. 3. Graphical solution of Eqs. (3), showing the case in which the transition is second order. The straight lines are Eq. (3b) for different values of T, and the curve is a plot of the solutions of (3a') for $\Delta' < 0.3662$.



FIG. 4. Graphical solution of Eqs. (3) for $0.4 < \Delta' < 0.5$, showing a first-order transition. The plot of the solutions of Eq. (3a') here has two branches: Of the two intersections of the straight lines with these curves one corresponds to a maximum of the free energy and the other corresponds to a minimum.

tion of magnetization and temperature. This is easily found with the help of the expression

$$G(M,T) = -kT \ln Z + \int H dM,$$
$$= -kT \ln Z + \frac{1}{2} \lambda M^{2}.$$

On substituting Eq. (1) for Z with $H=\lambda M$, writing $\tau=kT/\Delta$, and using the dimensionless quantities M' and Δ' introduced above, we find

$$\frac{1}{\Delta} (G(M',\tau) - G(0,\tau)) = -\tau \ln \left(\frac{1 + e^{-1/\tau} (1 + e^{M'/\tau\Delta'} + e^{-M'/\tau\Delta'})}{1 + 3e^{-1/\tau}} \right) + \frac{1}{2\Delta'} M'^2. \quad (4)$$

The free energy is a minimum for the equilibrium state of the system. In Fig. 6, Eq. (4) is plotted as a function of M' for different values of τ and for $\Delta'=0.43$. We see that for $\tau=0.58$ the absolute minimum of the free energy occurs at M'=0.7. As the temperature is raised the minimum moves inward until, for $\tau=0.6$, the minimum for M'=0 and that for M'=0.7 have the same free energy, so the two phases will coexist at this point. As the temperature is increased the state with M'=0becomes the absolute minimum, although the magnetized state is metastable. Finally, at temperatures above $\tau=0.63$ the only stable state is the unmagnetized one. The two minima and the maximum in these curves correspond to the three solutions of Eqs. (3) shown graphically in Fig. 4.

In Fig. 7, similar curves are shown for $\Delta'=0.39$. Here there are three types of curves. At temperatures above $\tau=0.790$ the only extremum in the free-energy-magnetization curve is for the unmagnetized state

520



FIG. 5. Graphical solution of Eqs. 3 for $0.3662 < \Delta' < 0.4$. The graph of the solutions of (3a') has a curvature near x=0 which produces a first-order transition.

M'=0. This corresponds to curve (c) in Fig. 5. For $0.770 < \tau < 0.790$ there are two minima and one maximum, corresponding to curve (b) in Fig. 5. In this region, for $\tau > 0.786$, the minimum at M'=0 is the absolute minimum, and the nonmagnetic state is the stable state. For $\tau < 0.786$ the magnetic state is absolutely stable. Below $\tau = 0.770$ the extremum at the origin is a maximum, and only the magnetic state is stable. These curves correspond to (a) in Fig. 5.

In each of these cases there is a discontinuous jump in the magnetization at a critical temperature. The existence of metastable states provides the possibility of thermal hysteresis effects and indeed, for $\Delta' > 0.4$, it is possible that the nonmagnetic state can be observed at arbitrarily low temperatures. For $\Delta'=0.38$, however, metastable states can be found only in a temperature range $\Delta \tau \sim 0.005T_e$, so that hysteresis would be difficult to find here. It should be emphasized that these state-



FIG. 6. Graph of the free energy as a function of magnetization for different values of the temperature, for $\Delta'=0.43$. As the temperature is raised from the lowest value shown, the minimum moves inward and upward until the free energy of the minimum with $M'\neq 0$ is higher than the minimum with M'=0, when a first-order transition occurs.

ments are based on a molecular-field approximation, and the extent to which a more accurate theory would modify these conclusions is not clear. The observability of hysteresis effects depends also upon the kinetics of the ordering process. We may note from Figs. 6 and 7 that the energy barriers separating the relative from the absolute minimum are $\approx 0.005\Delta$. For UO₂, $\Delta \sim 50^{\circ}$ K would produce, on this theory, the correct discontinuity in the magnetization and the correct transition temperature. The barriers are then $\leq 0.025^{\circ}$ K, so that we may anticipate, with any reasonable nucleation process, a rapid transition from the metastable state to the absolutely stable one, and hysteresis effects may be difficult to observe. Such effects were not found by Frazer *et al.*

A further examination of the free energy gives a number of theorems about the nature of the phase transition. These theorems are summarized in Table I.



FIG. 7. Free energy versus M' for $\Delta'=0.39$, showing a first-order transition at $\tau_e=0.786$.

To show that there is no stable ordered state for $\Delta' > 0.5$, we consider the free energy [Eq. (4)] at very low temperatures. We find, for $\Delta' > 0$,

$$1/\Delta) (G(M',\tau) - G(0,\tau))$$

= $\gamma(M',\tau) \xrightarrow[\tau \to 0]{} - (M'/\Delta' - 1) + (1/2\Delta')M'^2 + \cdots$ (5)

In order to have a magnetic state at low temperatures, this quantity must have a minimum, at a nonzero value of M', such that $\gamma_{\min}(M',\tau) < 0$. This requires (for M'=1)

$$-(1/2\Delta')+1<0, \text{ or } \Delta'<\frac{1}{2}.$$
 (6)

If we require a minimum at M' < 1, the condition on Δ' is still more stringent. Hence, as stated in the table, all nonzero solutions of Eqs. (3) for $0.5 < \Delta' < 1.0$ are unstable relative to the unmagnetized state. (It has been

or

TABLE I. Summary of the properties of the transition for different values of the ratio Δ' of the crystal-field splitting to the exchange splitting.

∆′>0.5	No stable magnetically ordered state at any temperature
0.3662<∆′<0.5	Magnetic state; first-order phase transition. Discontinuity in magnetization at critical temperature varies from 1.0 at $\Delta'=0.5$ to 0 at $\Delta'=0.3662$.
∆′<0.3662	Magnetic state; second-order phase tran- sition. Critical temperature given by $\Delta' \tau_e(e^{1/\tau_e}+3)=2$.

assumed that the external magnetic field is zero. Such a field could stabilize a magnetic phase in a ferromagnet.)

We have seen above that the phase transition is of the first order for $\Delta' < 0.5$. Numerical solution of the equations for M' show that the discontinuity in the magnetization at the transition temperature drops from 100% at $\Delta'=0.5$ to zero at $\Delta'=0.36$. To find the lower limit of this region of first-order transitions and to prove the remaining theorems in the table, we must consider the behavior of the free energy in the vicinity of M'=0. We find

$$\gamma(M',\tau) \underset{M' \to 0}{\longrightarrow} \left(-\frac{\tau}{e^{1/\tau} + 3} \left(\frac{1}{\Delta' \tau} \right)^2 + \frac{1}{2\Delta'} \right) M'^2 + \left(-\frac{\tau}{12(e^{1/\tau} + 3)} \left(\frac{1}{\Delta' \tau} \right)^4 + \frac{\tau}{2(e^{1/\tau} + 3)^2} \left(\frac{1}{\Delta' \tau} \right)^4 \right) M'^4 + \cdots$$
(7)

According to the theory of Landau-Lifshitz,¹³ the critical point in a second-order phase transition is determined by the vanishing of the coefficient of M'^2 in (7), provided that the coefficient of M'^4 is positive. Geometrically, the vanishing of the coefficient of M'^2 corresponds to the maximum at M'=0 becoming a minimum of $\gamma(M',\tau)$. Such changes also occur in first-order transitions, as is seen in Fig. 7, but the minimum at the origin is only metastable in this case, and it is necessary that the coefficient of M'^4 be positive if the transition is to be of second order. The vanishing of the coefficient of M'^2 at $\tau = \tau_c$ leads to the condition

$$\Delta' \tau_c (e^{1/\tau_c} + 3) = 2 \tag{8}$$

for the critical temperature for those values of Δ' for which the phase change is of second order. This range is defined by the condition on the coefficient of M'^4 . We have

$$-\frac{\tau_{c}}{12(e^{1/\tau_{c}}+3)} \left(\frac{1}{\Delta'\tau_{c}}\right)^{4} + \frac{\tau_{c}}{2(e^{1/\tau_{c}}+3)^{2}} \left(\frac{1}{\Delta'\tau_{c}}\right)^{4} = 0, \quad (9)$$

¹³ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Inc., New York, 1958), p. 430.

which implies

$$e^{1/\tau_c}=3$$
, (10)

$$\tau_c = 1/\ln 3. \tag{11}$$

Combining (10) and (11) with (8) and noting that τ_{e} decreases as Δ' increases, we require

$$\Delta' < \frac{1}{3} \ln 3 = 0.36620 \tag{12}$$

for a second-order transition, as is indicated in Table I. In the second-order region, the behavior of the magnetization as a function of temperature is different from that of the Brillouin function for spin 1, in that the magnetization remains higher as $T/T_c \rightarrow 1$. As $\Delta' \rightarrow -\infty$, the steepness of the falloff of M' with T/T_c is reduced, and the normal Brillouin behavior is obtained. In the firstorder region the calculations have been done by numerical minimization of the free energy. In Fig. 8 we show τ_c and M_c (the discontinuity in the magnetization at the critical temperature) as a function of Δ' . These quantities are defined, for a first-order transition, by the conditions

$$\frac{\partial [\gamma(M_{c},\tau_{c})]}{\partial M} = 0,$$

$$\gamma(M_{c},\tau_{c}) = 0.$$
(13)

We have considered the determination of the magnetization as a function of the temperature for the case of a ferromagnet. It is clear from the treatment of Anderson¹⁴ that for a face-centered cubic antiferromagnet with type-I structure (as found for UO₂ by Frazer *et al.*) the behavior of the sublattice magnetization versus *T* is exactly the same as for a ferromagnet, and the thermodynamic treatment is indentical for positive or negative exchange interactions. A plot of *M'* versus T/T_c is shown in Fig. 9 for $\Delta'=0.39$ and $\Delta'=0.43$. Also shown are the experimental results of Ref. 1. The agreement, for $\Delta'=0.43$, is quite good, probably better than could be expected from a molecular-field model. For $\Delta'=0.43$ the critical temperature was found to be



FIG. 8. Critical temperature τ_{o} and value of the magnetization M_{o}' at this temperature versus Δ' . Below $\Delta'=0.3662 M_{o}'=0$ and the transition is second order. Above $\Delta'=0.5$ no ordering occurs.

¹⁴ P. W. Anderson, Phys. Rev. 79, 705 (1950).

 $\tau_c = kT_c/\Delta = 0.60$, so that the triplet level is expected to lie at $\Delta = kT_c/0.6 \approx 50^{\circ}$ K for paramagnetic UO₂, since T_c is found experimentally to be $\approx 30^{\circ}$ K. A far infrared measurement to test the validity of this prediction would be worthwhile.

IV. SUSCEPTIBILITY AND LATENT HEAT

The magnetic susceptibility of UO₂ can be calculated on our model by following the procedures of Anderson¹⁴ and Van Vleck.¹⁵ The face-centered cubic lattice is divided into four sublattices such that the nearest neighbor of a point on one sublattice consists of four points on each of the remaining three sublattices (Fig. 1 of Ref. 14). The magnetic moment per atom induced in sublattice n ($n=1, \dots, 4$) is

$$M_{n} = g\mu_{\rm B} \frac{e^{g\mu_{\rm B}H_{n}/kT} - e^{-g\mu_{\rm B}H_{n}/kT}}{e^{\Delta/kT} + 1 + e^{g\mu_{\rm B}H_{n}/kT} + e^{-g\mu_{\rm B}H_{n}/kT}}, \quad (14)$$

as follows from Eq. (2). Here H_n is the magnetic field acting on the *n*th sublattice, given by

$$H_n = H - \lambda \sum_{m \neq n} M_m, \qquad (15)$$

where an interaction only between nearest neighbors has been assumed. The constant λ is related to the nearest-neighbor exchange integral J by $\lambda = 2JZ/(g\mu_{\rm B})^2$, where Z is the number of neighbors on an adjacent sublattice (Z=4 for UO₂). For $T > T_c$ we expand the exponential in (15) to obtain

 $M_n = \frac{2(g\mu_B)^2}{kT} \frac{H_n}{(e^{\Delta/kT} + 3)},$

and

$$M = \frac{1}{4} \sum_{n} M_{n} = \frac{1}{4} \frac{2(g\mu_{\rm B})^{2}}{kT(e^{\Delta/kT} + 3)} \sum_{n} H_{n}$$
$$= \frac{2(g\mu_{\rm B})^{2}}{kT(e^{\Delta/kT} + 3)} (H - 3\lambda M)$$
$$= \frac{2(g\mu_{\rm B})^{2}}{kT(e^{\Delta/kT} + 3) + 6\lambda(g\mu_{\rm B})^{2}} H, \qquad (17)$$

where M is the average magnetic moment per atom. The susceptibility is then given by

$$\chi = N(M/H) = \frac{2(g\mu_{\rm B})^2 N}{kT(e^{\Delta/kT} + 3) + 6\lambda(g\mu_{\rm B})^2},$$
(18)

where N is the number of atoms in the crystal. For $\Delta \ll kT$ this reduces to a Curie-Weiss law,

$$\chi \approx \frac{\frac{1}{2} (g\mu_{\rm B})^2 N}{kT + \frac{3}{2} \lambda (g\mu_{\rm B})^2 + \frac{1}{4} \Delta}, \qquad (19)$$

¹⁵ J. H. Van Vleck, J. Chem. Phys. 9, 85 (1941).



FIG. 9. Magnetization versus T/T_e for $\Delta'=0.43$ and $\Delta'=0.39$. The circles are experimental points taken from Ref. 1. They fall quite close to the curve for $\Delta'=0.43$.

with the Curie-Weiss constant altered by the term $\frac{1}{4}\Delta$. At the critical temperature, however, the condition $\Delta \ll kT_e$ may not hold. In that case, $e^{\Delta/kT} > 1 + \Delta/kT$, and the susceptibility at T_e will be lower than an extrapolation from high temperature (assuming Curie-Weiss behavior) would indicate.

The susceptibility below the transition temperature is calculated for the separate cases (a) external field parallel to axis of antiferromagnetism and (b) external field perpendicular to this axis. For case (a) we start with Eq. (14) and write

$$M_n = M_n^0 + \delta M_n,$$

$$H_n = H_n^0 + \delta H_n,$$
(20)

where

φ

(16)

$$\delta H_n = H - \lambda \sum_{m \neq n} \delta M_m,$$

$$H_n^0 = -\lambda \sum_{m \neq n} M_m^0 = +\lambda M_n^0,$$

and where M_n^0 is the equilibrium sublattice magnetization in the absence of an external field. Expanding (14) in a series in δH_n , we find

$$\delta M_{n} \approx \frac{(g\mu_{\rm B})^{2}}{kT} - \frac{e^{g\mu_{\rm B}H_{n}0/kT} + e^{-g\mu_{\rm B}H_{n}0/kT}}{e^{\Delta/kT} + 1 + e^{g\mu_{\rm B}H_{n}0/kT} + e^{-g\mu_{\rm B}H_{n}0/kT}} \delta H_{n} - \frac{(M_{n}^{0})^{2}}{kT} \delta H_{n}. \quad (21)$$

For the magnetic structure under consideration, $(M_n^0)^2$ and

$$(T) = (e^{g\mu BHn^{0}/kT} + e^{-g\mu BHn^{0}/kT})/(e^{\Delta/kT} + 1 + e^{g\mu BHn^{0}/kT} + e^{-g\mu BHn^{0}/kT})$$

are independent of the particular sublattice, since the field and magnetization of the sublattices differ from one another only in sign. The additional magnetization per atom induced by the external field is then

$$M = \frac{1}{4} \sum_{n} \delta M_{n} = (1/kT) (\varphi(T) - (M_{n}^{0})^{2}) \frac{1}{4} \sum_{n} \delta H_{n},$$

= (1/kT) (\varphi(T) - (M_{n}^{0})^{2}) (H - 3\lambda M), (22)

so that the susceptibility (for the external field parallel to the magnetization) is

$$\chi_{11} = \frac{(\varphi(T) - (M_n^0)^2)N}{kT + 3\lambda(\varphi(T) - (M_n^0)^2)}.$$
 (23)

As $T \to 0$, χ_{11} vanishes, and above the transition temperature, where $M_n^0 = 0$, χ_{11} reduces to Eq. (18).

The perpendicular susceptibility [case (b)] is obtained by requiring the induced magnetization of a sublattice to be parallel to the net field on the sublattice:

$$\delta M_n = |M_n^0| \left(\delta H_n / |H_n^0| \right) = (1/\lambda) \delta H_n,$$

so that

524

$$M = \frac{1}{4\lambda} \sum_{n} \delta H_{n} = \frac{1}{\lambda} (H - 3\lambda M),$$

and

$$X_{1} = N/4\lambda.$$
 (24)

For a crystal with randomly oriented domains, or for a powder sample the susceptibility for $T < T_e$ is

$$\chi = \frac{2}{3}\chi_{11} + \frac{1}{3}\chi_{1}.$$
 (25)

If the phase change is second order the sublattice magnetization is zero at $T=T_c$. It then follows from (8), (25), and (18) that the susceptibility is continuous, as expected, at a second-order phase change, and that $\chi(T=0)=\frac{2}{3}\chi(T=T_c)$, as was found by Van Vleck. In the case of a first-order transition, however, M_n^0 is not zero at T_c and there is a discontinuity in the susceptibility.

The susceptibility of UO_2 has been measured by Trzebiatowski and Selwood,¹⁶ by Arrott and Goldman,¹⁷ and by Leask, Roberts, Walter, and Wolf.¹⁸ The results are typical of antiferromagnets in showing a peak at the Néel temperature and a drop to a constant value as $T \rightarrow 0$. The theoretical results presented here match this behavior qualitatively, as do all theoretical calculations for simple antiferromagnets, but the quantitative agreement is poor, being as much as a factor of 2 too low as $T \rightarrow 0$. The agreement can be improved by choosing parameters other than $\Delta' = 0.43$ and $\Delta \approx 50^{\circ}$ K, but then the agreement with the magnetization curve is worsened. It can be argued that detailed agreement for the magnetization is not to be expected on the molecular-field theory or, alternately, that the simple theory assuming only nearest-neighbor exchange interactions is inadequate. In any event, we are left with a quantitative discrepancy, although the qualitative features of the transition are clearly displayed.

We consider finally the latent heat of the first-order transition. This is easily calculated from Eq. (4) for the free energy by noting that the entropy S is given by

$$S(M,T) = (\partial G/\partial T)_M$$

and the latent heat L per magnetic ion is

$$L = T_c(S(0,T_c) - S(M_c,T_c)).$$

The calculation then gives

$$\frac{L}{\Delta} = \frac{M_{c'}^{2}}{2\Delta'} + \frac{3}{e^{1/\tau_{c}} + 3} - \frac{1 + e^{M_{c'}/\Delta'\tau_{c}} + e^{-M_{c}/\Delta'\tau_{c}}}{e^{1/\tau_{c}} + 1 + e^{M_{c'}/\Delta'\tau_{c}} + e^{-M_{c'}/\Delta'\tau_{c}}}.$$
 (26)

For $\Delta'=0.43$, $M_e'=0.7$, $\Delta=50^{\circ}$ K, and $\tau_e=0.6$, this is $\approx 1.4 \times 10^{-2}$ kcal/mole or about 10^{-4} times the latent heat for a solid-liquid transition.

V. CONCLUSION

The model presented here gives a qualitative picture similar to that observed experimentally in UO2. In addition, it gives simple picture of a first-order transition. In this respect it is similar to the first-order transition found theoretically by Bragg and Williams19 in their treatment of order-disorder phenomena in alloys of the type A_3B . The crossing of magnetic and nonmagnetic levels brought about by the self-consistent field shows more clearly in the present case the physical reason for the first-order change. A number of further experiments on UO2 are suggested by the theory. First, a far infrared investigation in the paramagnetic and antiferromagnetic regions should be able to test the validity of the assumption that the Γ_1 singlet lies lowest. Also, neutron-scattering experiments near the transition temperature in the presence of magnetic fields and at high pressures should show the effects of the variation of Δ' and Δ on the magnetization curve. Measurements on UO₂ diluted with thorium are also indicated.

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 ¹⁸ M. J. M. Leask, L. E. J. Roberts, A. J. Walter, and W. P. Wolf, J. Chem. Soc. (London) 75, 4788 (1963).

¹⁹ W. L. Bragg and E. J. Williams, Proc. Roy. Soc. (London) A145, 699 (1934).