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Theory of Magnetic-Moment-Jump Phase Transition with Application to UP[†]

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The simple Heisenberg exchange Hamiltonian $H_{12}=J\vec{S}_1\cdot\vec{S}_2$ may not represent the interaction between magnetic ions in a crystal well enough to permit a prediction of even the qualitative features of the magnetic properties. When the electric charge densities of the magnetic ions are nonspherical because of crystal field and spin-orbit interactions, the magnetic ions are coupled by electrostatic multipole interactions (EMI). When the temperature is such that there are states of different multipole moments being thermally populated, EMI can have a qualitative effect on the temperature dependence of the magnetic properties. In this paper, we show that in the molecular-field approximation, the Hamiltonian consisting of only the crystal-field potential and the Heisenberg exchange energy cannot account for the moment-jump phase transition observed in antiferromagnetic uranium monophosphide (UP). We develop a molecular-field theory including the quadrupole-quadrupole interaction term of the EMI and show how this theory can predict the moment-jump phase transition. Finally, we describe a calculation based on this theory and obtain the low-temperature behavior of the sublattice magnetization including the moment jump observed in UP.

I. INTRODUCTION

High-degree electrostatic and exchange interactions in magnetic crystals have drawn considerable attention in recent years.[1] It is now generally accepted that the simple Heisenberg exchange Hamiltonian may not adequately represent the interactions among magnetic ions when the orbital contributions to the magnetic moments are considerable. Indeed, magnetic ions are coupled by electric multipole interactions (EMI) whenever their electric charge densities are nonspherical because of crystal-field and spin-orbit interactions. When the crystal field and temperature are such that there are states of different charge densities being populated, EMI can have a large effect on the temperature dependence of the magnetic properties.

The electric-quadrupole-interaction (EQI) term of EMI has been invoked to account for the anomalous specific heat observed in cerium ethylsulphate[2] and to account for various optical-energy transfer processes.[3] Very recently Allen[4] showed that an effective quadrupole-quadrupole interaction due to virtual phonon coupling can give the sharp decrease of sublattice magnetization observed in UO_2. In all this work, it has been assumed that the EQI is the only non-negligible term of EMI. Baker *et al.* showed that this assumption is correct for Ce^{+3} pairs in $LaCl_3$ and $LaBr_3$.[5] This assumption may not be correct, however, because the higher-degree terms may be enhanced by electrostatic shielding and induced-moment effects.[6] At the present time, a detailed calculation of the relative strengths of the terms in the EMI is a prohibitively difficult task. More experimental and theoretical studies are needed to determine the strengths of the EMI terms and their effects on the magnetic and thermal properties of materials.

In this paper we report a new and drastic effect of EQI on the magnetic properties of a class of magnetically ordered crystals.[7] In particular, we show that the interesting phase transition recently observed in uranium monophosphide (UP)[8,9] in which the moments of the uranium ions undergo a discontinuous jump from 1.95 to $1.70\mu_B$, can be accounted for by adding the EQI term to the usual Hamiltonian consisting of the electrostatic crystal-field potential and the Heisenberg exchange term.

In the special case of crystals of high symmetry, the presence of magnetic order can lower the symmetry of the charge densities, causing qualitative changes in the energy-level structure of the magnetic ions. This change in symmetry can have a large effect on the magnetic properties of the material.

A discontinuous change of the magnetization as temperature increases can occur in the absence of EQI if the crystal-field and exchange interactions are appropriate. The condition is that the two lowest energy levels cross on a plot of energy vs molecular field. If the two levels cross at some value of molecular field H_c, then for a molecular field greater than H_c, the state of higher magnetic moment has lower energy. Suppose at $T=0$ the exchange interaction is large enough to give a molecular field greater than H_c, then each ion has the higher moment. As the temperature increases, the state of higher energy (and lower moment) becomes populated. This lowers the thermal average of the magnetic moment so that the molecular field is lowered, approaching H_c. This causes the energy difference to be reduced and the whole process to be accelerated. Because of the self-consistent nature of the molecular field, this process can give a moment-jump phase transition. However, this theory cannot account for the transition that is observed in UP. It gives much too low a transition temperature for all reasonable strengths of the crystal-field and exchange interactions. In this model, the energy changes of the states taking place during the transition are changes in magnetic energy. When the EQI is included, the energy levels are determined by both the molecular field and the electrostatic "quadrupole field" in a self-consistent manner. In this case, the energy changes taking place at the transition can be mainly electrostatic. It is this essential difference that makes it possible for the theory that includes EQI to predict the kind of phase transition observed in UP.

In Sec. II we derive an approximate single-ion Hamiltonian including the EQI for a magnetically ordered crystal. In Sec. III we simplify the problem to include only two states, each of which possesses a constant magnetic moment and electric quadrupole moment. Using these simplifications, we can display the physical aspects of this calculation and the role played by EQI in the phase transition. In Sec. IV we describe a numerical calculation on antiferromagnetic UP and show that EQI can account for the anomalous temperature dependence of the magnetization at low temperature. However, because of the many unknown quantities involved in the crystal-field and spin-orbit interactions, our calculation must be regarded as only an indication of the importance of EQI in UP and other magnetically ordered crystals with large orbital contribution to the magnetic moment rather than a determination of the crystal-field parameters and strength of the EQI in UP.

II. SINGLE-ION HAMILTONIAN

We consider the Hamiltonian

$$\mathcal{H}=\sum_i V_{ci}-\frac{1}{2}\sum_{i,j}\mathcal{J}_{ij}\vec{J}_i\cdot\vec{J}_j-\frac{1}{2}\sum_{i,j}K_{ij}Q_iQ_j\ . \qquad (2.1)$$

Here, V_{ci} is the single-ion crystal-field potential, $\vec{J}_i$ is the total angular momentum of the magnetic ion at the ith site, and $Q_i=3(J_i^z)^2-J(J+1)$ is the quadruple-moment operator. (Throughout this work, the quadrupole moment is defined as above with the proportionality constant included in the coupling-strength parameter K_{ij}.) $\mathcal{J}_{ij}$ and K_{ij} represent the Heisenberg exchange and the EQI coupling parameters, respectively. In Eq. (2.1) the off-diagonal terms of the EQI have been omitted. This is consistent with the EQI being small compared to the *cubic* crystal-field interaction with the approximation made in the following. In the ordered phase we split the total Hamiltonian into two parts as

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1\ , \qquad (2.2)$$

where

$$\mathcal{H}_0=\sum_i\left[V_{ci}-\mathcal{J}(0)\langle J^z\rangle J_i^z-K(0)\langle Q\rangle Q_i\right]+\tfrac{1}{2}N\mathcal{J}(0)\langle J^z\rangle^2+\tfrac{1}{2}NK(0)\langle Q\rangle^2 \qquad (2.3)$$

and

$$\mathcal{H}_1=-\tfrac{1}{2}\sum_{i,j}\left(\mathcal{J}_{ij}\vec{j}_i\cdot\vec{j}_j+K_{ij}q_iq_j\right), \qquad (2.4)$$

with the definitions

$$\vec{j}_i=\vec{J}_i-\langle J^z\rangle\hat{z}\ , \qquad (2.5a)$$

$$q_i=Q_i-\langle Q\rangle\ , \qquad (2.5b)$$

and

$$\mathcal{J}(0)=\textstyle\sum_i\mathcal{J}_{ij}\ , \qquad (2.6a)$$

$$K(0)=\textstyle\sum_iK_{ij}\ . \qquad (2.6b)$$

$\mathcal{H}_0$ is the single-ion Hamiltonian describing the system in the ordered state in a "molecular-field" approximation including EQI. In Eq. (2.5), $\langle J^z\rangle$ and $\langle Q\rangle$ are, respectively, the thermal averages of the angular momentum and quadrupole moment per ion, and $\hat{z}$ denotes a unit vector in the z direction, the axis of moment ordering. We shall not be concerned with $\mathcal{H}_1$, though it gives collective excitations and is important in calculation of the various thermodynamic quantities. The single-ion Hamiltonian $\mathcal{H}_0$ derived above should describe the system to a satisfactory approximation for all our purposes. It is to be noted that the nonoperator terms appearing in $\mathcal{H}_0$ shift all the energy levels by the same amount. This shift is temperature dependent so that these terms must be included in a calculation of the thermodynamic potentials.

III. TWO-LEVEL MODEL OF CONSTANT MOMENTS AND MOMENT-JUMP PHASE TRANSITION

Using the single-ion Hamiltonian derived in Sec. II, we now show how a moment-jump phase transition can occur as temperature increases. We simplify the problem so that a graphical method can be used to solve the self-consistent equations.

Consider the case in which only two states are populated throughout the temperature range of interest. Assume that the magnetic moments μ_1,

μ_2 and the quadrupole moments Q_1, Q_2 of the two levels remain unchanged in our discussion and that the two states are not coupled by $\mathcal{H}$.

Then the thermal averages $\langle\mu\rangle$ and $\langle Q\rangle$ of the system are

$$\langle\mu\rangle = \tfrac{1}{2}(\mu_1+\mu_2)+\tfrac{1}{2}(\mu_1-\mu_2)\tanh(\epsilon/2kT), \tag{3.1}$$

$$\langle Q\rangle = \tfrac{1}{2}(Q_1+Q_2)+\tfrac{1}{2}(Q_1+Q_2)\tanh(\epsilon/2kT), \tag{3.2}$$

where

$$\epsilon=\epsilon_2-\epsilon_1 \tag{3.3a}$$

is the energy difference of the two states and can be written as

$$\epsilon=\lambda(\mu_1-\mu_2)\langle\mu\rangle+\alpha(Q_1-Q_2)\langle Q\rangle+\epsilon_0. \tag{3.3b}$$

Here $\lambda=\mathcal{J}(0)/g_J^2$ is the usual molecular-field constant, $\alpha=K(0)$ measures the strength of EQI, and ϵ_0 is the energy difference of the two energy levels in the absence of exchange interaction and EQI, i.e., when $\lambda=\alpha=0$.

From Eqs. (3.1) and (3.2), we see that $\langle\mu\rangle$ and $\langle Q\rangle$ are linearly related and we can write $\langle Q\rangle$ as a linear function of $\langle\mu\rangle$:

$$\langle Q\rangle=\tfrac{1}{2}(Q_1+Q_2)+\tfrac{1}{2}(Q_1-Q_2)[\langle\mu\rangle-\tfrac{1}{2}(\mu_1+\mu_2)]. \tag{3.4}$$

This enables us to express ϵ as a function of $\langle\mu\rangle$ alone. We obtain

$$\epsilon=a\langle\mu\rangle+b, \tag{3.5}$$

where

$$a=\lambda(\mu_1-\mu_2)+\alpha(Q_1-Q_2)^2/(\mu_1-\mu_2) \tag{3.6a}$$

and

$$b=\tfrac{1}{2}\alpha(Q_1-Q_2)[(Q_1+Q_2)-(Q_1-Q_2)(\mu_1+\mu_2)/(\mu_1-\mu_2)]+\epsilon_0. \tag{3.6b}$$

Equations (3.1) and (3.5) can then be solved graphically. First, the curve $\langle\mu\rangle$ is plotted as a function of $y=\epsilon/2kT$. Then for each value of temperature T, a straight line

$$\langle\mu\rangle=2kTy/a-b/a \tag{3.7}$$

is drawn on the same graph. [Note that Eq. (3.7) is the same relation as Eq. (3.5) written in terms of y instead of ϵ.] Without loss of generality we choose the labels such that $\mu_1>\mu_2$. This construction is shown in Fig. 1. The intersections of the line and the curve give the self-consistent solution $\langle\mu\rangle$ for each temperature, and from Eq. (3.4) one obtains $\langle Q\rangle$.

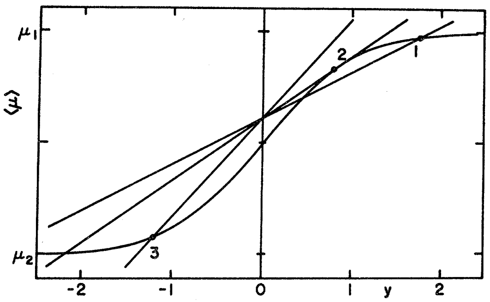

FIG. 1. Graphical solution of the self-consistent equations resulting from the two-level model of constant moments. The solutions are shown for temperatures (1) below the transition temperature, (2) at the transition temperature, and (3) above the transition temperature

If the $y=0$ intercept of the straight line is greater than $\frac{1}{2}(\mu_1+\mu_2)$ and less than μ_1, that is, if

$$\mu_1>-b/a>\tfrac{1}{2}(\mu_1+\mu_2), \tag{3.8}$$

a discontinuous decrease in the magnetization can occur when the temperature is raised. At low temperature, the slope of the line, $2kT/a$, is small and there are three intersections as shown in Fig. 1. Suppose that the solution of higher magnetic moment has lower free energy and therefore is the physical solution. Then the thermal-averaged magnetic moment per ion is nearly μ_1. As the temperature increases, the slope of the line increases and the intersection gives a lower value of $\langle\mu\rangle$. The magnetization drops gradually until the line is tangent to the curve. Any further increase in temperature causes the solution of the highest moment to disappear and the magnetization changes discontinuously to a value corresponding to the remaining intersection. From Fig. 1 it is seen that the magnetic moment per ion is then about μ_2. If the temperature is further raised, the magnetic moment per ion increases, approaching $\frac{1}{2}(\mu_1+\mu_2)$. This increase may never take place in reality since the higher-lying energy states are usually populated at this high temperature. The thermal-averaged magnetic moment per ion as a function of temperatures is displayed schematically in Fig. 2. A discontinuous *increase* in magnetic moment can occur in a similar way, but we restrict our discussion to a discontinuous decrease in magnetic moment as the temperature is raised.

In general, when more than one solution exists, it is essential to consider free energy. The physical solution is the one with the lowest magnetic Helmholtz free energy

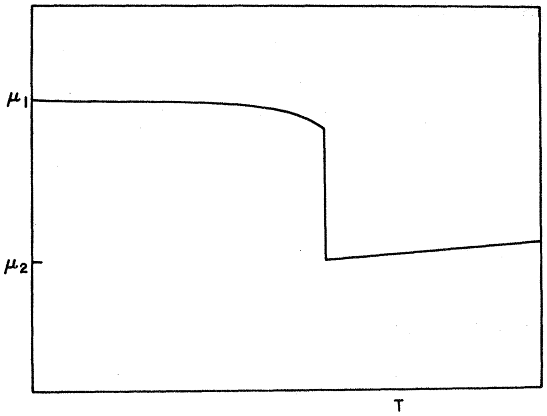

FIG. 2. Thermal-averaged magnetic moment as a function of temperature calculated using the graphical solutions of Fig. 1.

$$F = -kT \exp(\mathrm{tr}\, e^{(-\mathcal{H}_0/kT)}).$$

The free energies of the solutions can be such that the solution of lowest moment may become the physical solution at a temperature below the temperature required to cause the solution of highest moment to disappear.

We note also that the above discussion is quite general. It includes the Heisenberg exchange only interaction as a special case ($\alpha = 0$), and can be readily generalized to include high-degree multipole interactions. It is interesting to examine the case with Heisenberg exchange interaction only. As we discussed in Sec. I, this can also give a moment-jump phase transition.

Putting $\alpha = 0$ we obtain from Eq. (3.8) the condition for a discontinuous moment jump to occur:

$$\mu_1 > -\epsilon_0/\lambda(\mu_1 - \mu_2) > \tfrac{1}{2}(\mu_1 + \mu_2). \tag{3.9}$$

Notice that in this two-level model, at $T = 0$ the magnetic moment per ion is μ_1 and at $T = \infty$ it is $\frac{1}{2}(\mu_1 + \mu_2)$ for $\mu_1 > \mu_2$ as we assumed. To have Eq. (3.9) satisfied we first have to have the energy level of higher moment to be the higher level in the absence of molecular field. So $\epsilon_0 < 0$. Recall that the energy difference $\epsilon = \epsilon_2 - \epsilon_1$ is given as

$$\epsilon = \epsilon_0 + \lambda(\mu_1 - \mu_2)\langle\mu\rangle. \tag{3.10}$$

The inequality equation (3.9) simply states that two levels cross in the molecular field when the thermal-averaged moment decreases (as temperature increases) from μ_1 to $\frac{1}{2}(\mu_1 + \mu_2)$.

The upper limit of the critical temperature T_c at which the moment-jump phase transition occurs can be estimated from the slope of the curve of Eq. (3.1) at $y = 0$. The slope $d\langle\mu\rangle/dy\,|_{y=0}$ is $\frac{1}{2}(\mu_1 - \mu_2)$. Remember that a discontinuous change of the magnetic moment will occur if, in Fig. 1, the straight line is tangent to the curve at T_c. Consequently,

$$2kT_c/a < \tfrac{1}{2}(\mu_1 - \mu_2), \tag{3.11}$$

or, substituting Eq. (3.6a) for a,

$$2kT_c/\lambda(\mu_1 - \mu_2) < \tfrac{1}{2}(\mu_1 - \mu_2)\ . \tag{3.12}$$

The molecular-field constant λ can be estimated as

$$\lambda\mu_1^2 \sim kT_N\ . \tag{3.13}$$

We then have

$$T_c < [(\mu_1 - \mu_2)^2/4\mu_1^2]T_N\ . \tag{3.14}$$

For UP, $\mu_1 = 1.95\mu_B$, $\mu_2 = 1.70\mu_B$; this gives the moment-jump transition at

$$T_c < \tfrac{1}{256}T_N\ ; \tag{3.15}$$

with $T_N \simeq 125$ K, $T_c \cong \frac{1}{2}$ K, which is too low compared with the observed transition temperature of 23 K. It is also to be noted that in the limiting case given above, the thermal-averaged moment $\langle\mu\rangle$ would decline to almost $\frac{1}{2}(\mu_1 + \mu_2)$ before the transition took place. This is in contrast to the behavior in UP where $\langle\mu\rangle$ remains essentially constant up to the transition temperature. From the above analysis, we conclude that a theory that includes only the crystal-field and exchange interactions cannot account for the moment-jump phase transition that is observed in UP.

EQI is important in explaining the magnetic behavior of UP. The energy levels are now determined by the thermal-averaged magnetic moment $\langle\mu\rangle$ and electric quadrupole moment $\langle Q\rangle$ self-consistently. As discussed earlier, for $\alpha = 0$ the necessary condition for magnetization to change discontinuously, Eq. (3.8), is that the two levels cross in the molecular field. With $\alpha \neq 0$, the argument still applies. It may be clearer to rewrite Eq. (3.8) as

$$\begin{aligned}\epsilon_0 + \lambda\mu_1 i(\mu_1 - \mu_2) + \alpha Q_1(Q_1 - Q_2) > 0\\ > \epsilon_0 + \tfrac{1}{2}\lambda(\mu_1 + \mu_2)(\mu_1 - \mu_2)\\ + \tfrac{1}{2}\alpha(Q_1 + Q_2)(Q_1 - Q_2)\,.\end{aligned} \tag{3.16}$$

The quantity on the left-hand side is recognized as the energy difference $\epsilon_2 - \epsilon_1$ at $T = 0$ when $\langle\mu\rangle = \mu_1$ and the quantity on the right-hand side, the energy difference at $T = \infty$. The two levels, however, need not cross due to the exchange energy alone. EQI can play a major role in causing the levels to cross.

IV. URANIUM MONOPHOSPHIDE

In Sec. III, it was shown how EQI can give a moment-jump phase transition similar to that observed in UP. In this section, a more complete calculation including all ten states of the $J=\frac{9}{2}$ multiplet of the U^{3+} ion is described.[10] In this calculation, the moments of each state are temperature dependent in contrast to the calculation of Sec. III.

The magnetism in UP arises from a partially filled $5f$ shell of the uranium ion. According to Hund's rule, the U^{3+} ion has $S=\frac{3}{2}$, $L=6$, and $J=\frac{9}{2}$. We assume that the spin-orbit coupling is strong compared to the crystal-field interaction so that J is a good quantum number. Although it has been shown that in actinides the crystal field may be as strong as the spin-orbit coupling,[11] in the present case, to take this possibility into account would make the analysis of the problem unmanageable because of the lack of information about both the crystal-field and spin-orbit interactions in UP. Considering only the lowest J multiplet of states, the cubic crystal field can be written in terms of two parameters W and x as[12]

$$V_c = W\{x[O_4/F(4)] + (1-|x|)[O_6/F(6)]\} , \quad |x| \leq 1 \tag{4.1}$$

where O_4 and O_6 are the operator equivalents of the 4th- and 6th-degree terms of the crystal-field potential, and $F(4)$ and $F(6)$ are constant factors.

Since the crystal-field parameters W and x are unknown, we began with a preliminary study of the U^{3+} energy spectrum in the combined cubic crystal field and exchange molecular field. The Hamiltonian

$$H = V_c - hJ^z \tag{4.2}$$

was numerically diagonalized for a whole range of molecular field h. The energies and expectations values of J^z and Q were calculated for $W=1$ and $-1 \leq x \leq 1$. (For $W=-1$, the energy spectrum is simply inverted.) Of the great variety of energy schemes obtained, we focused our attention on those with the magnetic moments of the two lowest energy states approximately equal to the observed moments in UP at temperatures above and below the moment jump. This restricts our study to one in which the EQI is not strong enough to change the moments of the lowest states appreciably. (To calculate the magnetic moment, the Landé g factor for $J=\frac{9}{2}$, $g=\frac{8}{11}$ has been used in this work.)

To see the effect of the EQI on the energy spectra, the Hamiltonian

$$H = V_c - hJ^z - AQ \tag{4.3}$$

was diagonalized for a range of A. Since the magnetic moment in UP is observed to change only 11% at the moment jump, we keep the molecular field fixed in this preliminary calculation.

According to the simplified study described in Sec. III, a moment-jump phase transition may take place if the two lowest energy levels cross on a plot of energy vs A. When this level crossing occurred, the values of the four parameters W, x, λ, and α were deduced and used as the initial values in the full calculation described below.

The numerical calculation of the simultaneously self-consistent values of $\langle J^z\rangle$ and $\langle Q\rangle$ was carried out as follows. For each temperature, initial values of $\langle J^z\rangle$ and $\langle Q\rangle$ were chosen, and the Hamiltonian of Eq. (2.3) was diagonalized numerically. Then, improved values of the thermal averages were calculated using the resulting energies E_n and wave functions $|n\rangle$ according to

$$\langle J^z\rangle = (1/Z)\sum_n \langle n|J^z|n\rangle e^{-E_n/kT} , \tag{4.4}$$

$$\langle Q\rangle = (1/Z)\sum_n \langle n|Q|n\rangle e^{-E_n/kT} , \tag{4.5}$$

and

$$Z = \sum_n e^{-E_n/kT} . \tag{4.6}$$

Using these improved values, the Hamiltonian was diagonalized again and the whole process was iterated until satisfactory convergence was reached.

By choosing different initial values of $\langle J^z\rangle$ and $\langle Q\rangle$ the sequence described above could be made to converge on each of the double self-consistent solutions. The free energy was computed for each solution, and the one with the minimum value of F was taken as the physical solution.

The four parameters W, x, λ, and α were adjusted by visually comparing the computed magnetization curves to the magnetization curve of UP derived from NMR measurements.[9] Since the NMR frequency is proportional to the thermal-averaged magnetic moment $\langle\mu\rangle$, the frequency was scaled to agree with the value of $\langle\mu\rangle$ measured by neutron diffraction at 4.2 K. The best fit so obtained is displayed in Fig. 3.

The values of the four parameters giving the best fit are $W=-40.9$ K, $x=-0.68$, $\lambda=52.8$ K, and $\alpha=1.0$ K. The low-temperature behavior of the magnetization of UP has been reproduced very well as shown in Fig. 3. However, the rather sharp drop of magnetization observed experimentally near the Néel temperature (about 125 K) is not predicted by this theory. This lack of agreement may arise from the many assumptions and approximations made in the calculation. Among them, first, the assumption that the spin-orbit coupling is strong compared to the crystal-field interaction

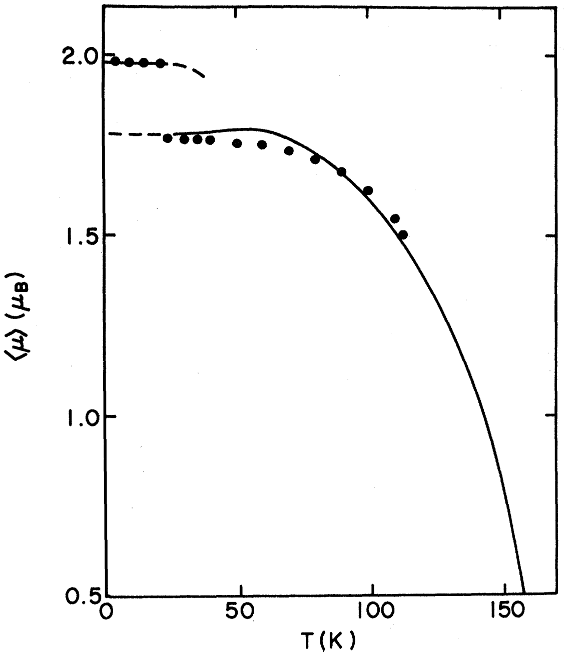

FIG. 3. Best fit of the theory (solid curve) to the scaled NMR data (solid circles). The broken curves represent the solutions of higher free energy.

may not be valid in UP. In fact, the total crystal-field energy-level splitting corresponding to the crystal-field parameters that give the best fit is 2860 K, while the spin-orbit coupling has been estimated to be of the same order[11]; and second, as mentioned in Sec. I, neglecting all the higher-degree terms in the EMI is not justified a *priori*. However, a refined calculation that takes these two effects into account is unwarranted at the present time because of the lack of experimental information.

The excellent agreement of the theory and experiment at low temperature does not imply that the values of the parameters that give the best fit actually characterize the substance, but rather indicates that the EMI can lead to anomalous temperature dependence of magnetization such as that observed in UP. A conclusive determination of the importance of EMI in magnetic properties of UP and other actinides will require further experimental and theoretical studies.

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