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Dynamical Jahn-Teller effect on UO_2

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The dynamical Jahn-Teller effect on UO_2 is investigated within a microscopic model including crystal-field effects, magnetic exchange, and linear coupling with a localized trigonal phonon mode acting on the Γ_5 symmetry ground state and the Γ_4 symmetry excited state. Numerical calculations are performed in order to determine the ordered-magnetic moment and the differential cross section of UO_2 at low temperature ($T < T_N$) following a properly implemented Lanczos recursion procedure. The Jahn-Teller coupling is found to be weak but essential to satisfactorily reproduce the experimental measurements.

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I. INTRODUCTION

Among all actinide compounds, uranium dioxide is one of the most studied, both theoretically[1–10] and experimentally.[11–18] This interest is due not only to technological motivations, for instance, its usage as nuclear fuel, but also for purely scientific reasons concerning the uranium electronic structure and for its magnetic anomalies. Uranium dioxide has a fluorite crystal structure with a U^{4+} ion at the center of a cube, surrounded by eight O^{2-} ions at the vertices. The electronic configuration of U^{4+} is $5f^2$, with f states well localized.[6,8] In a Russell-Saunders scheme, including spin-orbit interaction, its ground multiplet is a ninefold degenerate $^3H_4$ state with Landé factor $g(J,L,S)=0.8$. Following an intermediate-coupling (IC) approximation,[4] the ground multiplet of UO_2 is given by a combination of $^3H_4$, $^1G_4$, and $^3F_4$,[7] leading to an effective $g=0.8231$. The crystal field (CF) splits the $^3H_4'$ multiplet in a Γ_5 ground state (threefold degenerate) and in excited states Γ_3 (twofold degenerate), Γ_4 (threefold degenerate), and Γ_1 (singlet). Γ_i labels the irreducible representations of the cubic point group in the Koster notation.[19]

Experiments[11] and recent *ab initio* calculations[8] have confirmed that UO_2 is an antiferromagnet below $T_N=30.8$ K. Different magnetic orderings have been proposed, but recent experiments of inelastic neutron scattering with polarization analysis[16] and of NMR measurements[17] have indicated the existence (below T_N) of a 3-$\mathbf{k}$ structure. This magnetic ordering is consistent with an internal 3-$\mathbf{k}$ lattice distortion of $\delta=0.014$ Å, as revealed by the analysis of the neutron magnetic-scattering cross section measured at $T=4.2$ K by Faber *et al.*[13] For each U^{4+} ion, whose magnetic moment points along one of the diagonals of the cubic unit cell, there are two O^{2-} ions displaced forward or away from the center. As a result, the cubic symmetry of the crystal is maintained. A 3-$\mathbf{k}$ lattice distortion is also supported by *ab initio* calculations of Laskowski *et al.*[10] although the predicted distortion is larger than the experimental one.

Another interesting aspect associated with UO_2 is the reduction of the ordered moment in the antiferromagnetic phase. The calculated magnetic moment on Γ_5 states in IC approximation gives $\mu=2.06\mu_B$. Instead neutron-diffraction experiments measurements[13] at $T=4.2$ K gave $\mu=(1.74\pm0.02)\mu_B$. The problem of the reduction of the magnetic moment of UO_2 has been faced by various authors within different models which consider J-mixing induced by CF (Ref. 7) or a distortion of the oxygen cage surrounding the uranium ions[2,15] due to the coupled motion of electrons and lattice ions (static Jahn-Teller effect). However, the J mixing on the ground state is too weak to reduce satisfactorily the magnetic moment and the Allen's model[2] fails in a 3-$\mathbf{k}$ structure.[15]

Other useful information on UO_2 comes from neutron spectroscopy at different temperatures.[15] The neutron spectrum exhibits four peaks between 150 and 180 meV. The first of them, at 152.4 meV, was assigned to the $\Gamma_5\rightarrow\Gamma_3$ transition and the other ones to $\Gamma_5\rightarrow\Gamma_4$ transitions. A more resolved analysis near 152 meV revealed a further splitting into two peaks, interpreted as transitions towards the two rows of the Γ_3 level separated by a local magnetic exchange interaction.

To our knowledge a microscopic theory that coherently explains *all* the experimental facts is still lacking. In this paper we propose a simple model of dynamical Jahn-Teller (JT) effect to obtain the reduced ordered magnetic moment and to interpret the neutron spectra available below T_N. This should be a convenient starting point for more complex and general models. We study the dynamical JT effect on single U^{4+} ions considering a linear coupling of the orbital states of Γ_5 and Γ_4 symmetry with vibrational modes of t_2 symmetry. We also consider a magnetic exchange interaction and assume a 3-$\mathbf{k}$ structure, which seems the most likely on the basis of neutron-scattering experiments and theoretical works. The calculations of the vibronic states are carried out within the framework of the Lanczos-recursion procedure[20–22] with a proper choice of the initial state. At the beginning, we determine the vibronic states of U^{4+} ions involved in the calculation of the ordered magnetic moment at $T=4.2$ K. Then we calculate the differential cross section in dipole approximation, and we propose to interpret the experimental spectra as due to transitions from the ground vibronic

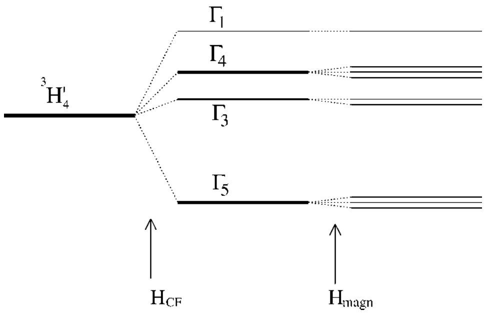

FIG. 1. Levels splitting produced by crystal-field and local magnetic interaction.

state of predominantly Γ_5 symmetry to excited vibronic states of mixed Γ_4 and Γ_3 symmetries.

In Sec. II the model Hamiltonian and the calculation procedure is described. Section III contains the results compared with the experimental measurements. In Sec. IV a brief discussion and conclusive notes are carried out.

II. MODEL HAMILTONIAN

In the intermediate-coupling (IC) approximation, useful for the description of the actinides, the electronic levels produced by electrostatic, spin-orbit, and correlation interaction[7] are a linear combination of multiplets with the same J but different L and S. The ground state calculated by Rahman and called $^3H'_4$, is

$$^3H'_4 = 0.9459\,^3H_4 - 0.3113\,^1G_4 + 0.0911\,^3F_4. \tag{1}$$

In this way, the Landé factor ($g=0.8$ in the Russell-Saunders approximation) assumes an effective value of 0.8231 in IC. The ground state $^3H'_4$ is split by a cubic CF, since UO_2 crystallizes in a fluorite-structure type where the U^{4+} ion is at the center of a cube whose corners are occupied by oxygen atoms. The lower state has Γ_5 symmetry, then in the order of increasing energy, we find levels of Γ_3, Γ_4, and Γ_1 symmetry (see Fig. 1). The crystal-field Hamiltonian, using the notation of Lea *et al.*,[23] is

$$H_{\mathrm{CF}} = W\left[x\left(\frac{O_4}{F(4)}\right) + (1-|x|)\left(\frac{O_6}{F(6)}\right)\right], \tag{2}$$

$O_4=O_4^0+5O_4^4$ and $O_6=O_6^0-21O_6^4$, O_n^m being the Stevens' operator equivalent. $F(4)$ and $F(6)$ are constant numbers for all states within a given J manifold[23] (here $J=4$, then $F(4)=60$ and $F(6)=1260$); W and x are CF parameters to be determined in such a way to reproduce the experimental level splitting of the $^3H'_4$ ground state. Depending on the approximations assumed in the eigenstates calculations, for UO_2 the parameters W and x have been found to be in the range 4.1–4.6 meV and 0.84–0.88, respectively.[15] It is worthwhile to notice that neither the CF operator nor the J mixing influence in a significant way the value of the ordered magnetic moment.[7] A molecular exchange field interaction $H_{magn}=-\boldsymbol{\mu}\cdot\mathbf{H}$, representing a local effective magnetic interaction with the ordered magnetic moments, removes completely the degeneracy as shown in the right part of Fig. 1. In a 3-**k** model the local mean field **H** is in the (1,1,1) direction, leading to

$$H_{magn} = -\boldsymbol{\mu}\cdot\mathbf{H} = \frac{h}{\sqrt{3}}(J_x + J_y + J_z), \tag{3}$$

with $h=g\mu_B H$. The value of h is not exactly known, but it has been estimated to be in the range of 1 meV and 1.6 meV,[15] in order to give values of the Neél temperature comparable with the experimental one.

The uranium ions present degenerate molecular orbitals (Γ_5, Γ_3, Γ_4), so a breakdown of the Born-Oppenheimer approximation[24] is expected and the electron-spin states can be coupled with molecular vibrations of proper symmetry, called JT active modes. In this system, the JT active modes are of a_1, e, and t_2 symmetry. The total symmetric mode a_1 produces only a line broadening[25] and is neglected here. A tetragonal e mode, for its simplicity, was taken into account by Sasaki and Obata[3] to describe the paramagnetic susceptibility and recently by Kolberg *et al.*[18] to interpret their measurements in mixed uranium-plutonium dioxides: however, a trigonal mode looks more appropriate for a 3-**k** structure.[9] So we consider a vibronic coupling among the Γ_5 and Γ_4 symmetries' orbital states and a t_2 vibrational mode. As usual in the study of JT systems, we work in a cluster model[26] where an effective mode alone is considered. The vibrational Hamiltonian H_v is taken in elastic approximation and written in a second quantization notation where a displacement is proportional to the sum of the creation and annihilation operator,

$$H_v(\Gamma_i) = \hbar\omega\left(a_x^\dagger a_x + a_y^\dagger a_y + a_z^\dagger a_z + \tfrac{3}{2}\right)P_{\Gamma_i}, \tag{4}$$

where P_{Γ_i} is the projector on the electronic eigenfunctions of symmetry Γ_i ($i=4,5$), and $\hbar\omega$ is the phonon energy for the t_2 mode, chosen here equal to 10 meV, a value in the range of measured transverse acoustical phonon energies.[12]

The JT interaction Hamiltonian can be written as

$$H_{\mathrm{JT}}(\Gamma_i) = \frac{\sqrt{3}}{2}\hbar\omega\sqrt{S(\Gamma_i)}\sum_{p=x,y,z}(a_p^\dagger + a_p)D_p P_{\Gamma_i}, \tag{5}$$

where $S(\Gamma_i)$ is the Huang-Rhys factor or the JT energy in units of the phonon energy and

$$D_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad D_y = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \qquad D_z = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{6}$$

are the Clebsh-Gordon coefficient matrices expressed on the basis of the electron-spin functions belonging to the Γ_i symmetry states. The Hamiltonians H_v and H_{JT} are understood as multiplied by the identity in the spin space.

At the end, the total Hamiltonian H_T that we consider includes on the same foot all the contributions here discussed and has the form,

$$H_T = H_{\mathrm{CF}} + H_{magn} + H_v(\Gamma_i) + H_{\mathrm{JT}}(\Gamma_i). \tag{7}$$

III. CALCULATION PROCEDURE

The basis functions for the system Hamiltonian in study are the direct product of the nine functions eigenstates of H_{CF}, partners of the irreducible representations Γ_5, Γ_3, Γ_4, Γ_1, and of the vibrational functions $|n_x,n_y,n_z\rangle$, where n_x, n_y, n_z label the phonon occupation numbers for the partners of the t_2 mode.

We have to take into account a high number of phonons[27] to explore large values of the Huang-Rhys factors. So the rank of the matrices to be handled could become too large for a direct diagonalization. However, a model with a linear JT coupling leads to a matrix Hamiltonian in a sparse form. In this situation we have found the Lanczos recursion method a very convenient and powerful procedure to determine with high precision the vibronic states of interest, usually the lower ones. More details can be found, for instance, in Refs. 28 and 29. An alternative approach, particularly convenient when the number of the recursion becomes too large, is constituted by the continued fractional expansion of the diagonal Green function matrix element $G_{00}(E)$, whose parameters are given by the coefficients (diagonal and off-diagonal) of the Lanczos chain.[22] The poles of the continued fraction give the eigenvalues of the vibronic system and their residua give the projected density of states which is immediately related to the optical spectra or to the differential cross section.

In order to determine the ordered magnetic moment, we have to calculate

$$\langle\mu\rangle = \sqrt{3}\langle\mu_z\rangle = \sqrt{3}g\mu_B\sum_n \rho_n\langle\Psi_n|J_z|\Psi_n\rangle, \tag{8}$$

where Ψ_n are the vibronic eigenstates and ρ_n are the corresponding Boltzmann population factors. In practice the vibronic states of interest are the lower ones determined with a two-pass Lanczos and choosing as the initial state of the Lanczos chain a zero-phonon state having as an orbital part one of the partner functions of the Γ_5 state.

For what concerns the differential cross section, let us remember that it can be written in dipole approximation and cubic symmetry,[30,31]

$$\frac{d^2\sigma}{d\Omega d\omega}\frac{k_i}{k_f} = \frac{1}{2}\left(\frac{\gamma e^2}{m_e c^2}g\right)^2 F^2(\mathbf{Q})\sum_{m,n}\rho_n|\langle\Psi_m|J_z|\Psi_n\rangle|^2 \times\delta(E_m-E_n-\hbar\omega), \tag{9}$$

where $|\Psi_n\rangle$ and $|\Psi_m\rangle$ are, respectively, the initial and final vibronic states of the transition, J_z is the component of the total angular momentum perpendicular to the scattering vector, $\mathbf{Q}$, $\mathbf{k_i}$, and $\mathbf{k_f}$ are neutron, initial, and final wave vectors, respectively, $F(\mathbf{Q})$ is the magnetic form factor, and $\hbar\omega$ is the neutron energy transfer $[\hbar\omega=(\hbar^2/2m)(k_f^2-k_i^2)]$.

Experiments are usually performed at small $\mathbf{Q}$ where $F^2(\mathbf{Q})\simeq 1$. So the main quantity to be calculated in the differential cross section (9) is the matrix elements modulus squared $|\langle\Psi_m|J_z|\Psi_n\rangle|^2$, which requires the knowledge of the vibronic functions $|\Psi_m\rangle$ and $|\Psi_n\rangle$. As suggested in our previous paper,[27] a proper choice of the seed state ϕ_0 of the Lanczos chain can simplify the calculations. In fact, if we choose

$$|\phi_0\rangle = \frac{J_z|\Psi_n\rangle}{\sqrt{\langle\Psi_n|J_z^2|\Psi_n\rangle}}, \tag{10}$$

we have

$$\langle\Psi_m|J_z|\Psi_n\rangle = \langle\Psi_m|\phi_0\rangle\sqrt{\langle\Psi_n|J_z^2|\Psi_n\rangle}. \tag{11}$$

Then the differential cross section is immediately given by the projection modulus squared of the vibronic states of interest $|\Psi_m\rangle$ on the initial state of the Lanczos chain, and the reconstruction with a two-pass Lanczos of all final states is so avoided.

IV. RESULTS

As outlined in the previous section, the states involved in the JT coupling with a trigonal phonon mode are those of Γ_5 and Γ_4 symmetry. It is worthwhile to notice that, in absence of JT coupling, the magnetic exchange interaction produces in each sublevel a certain mixing of the Γ_i states $(i=5,3,4,1)$. However, for the h values suggested in the literature for this system,[15] the component given by the CF contribution largely predominates. Then, for the sake of simplicity, in the following we continue to speak of Γ_i levels.

The energy separation between the ground Γ_5 level and the excited Γ_4 level is about 160 meV, a very large value compared to the energy of the transvarse-acoustic (TA) phonon modes ($\hbar\omega\approx 10$ meV at the border zone).[12] Therefore we expect that a JT coupling on the Γ_4 multiplet does not influence in a significant way the vibronic states coming from the Γ_5 multiplet. On the other hand the calculation of the ordered magnetic moment requires the knowledge of the lowest vibronic states only [see (8)], so, in order to calculate the ordered magnetic moment, we have found it convenient, as a starting point, to consider a JT coupling active only on the Γ_5 state. Then, in order to reproduce the experimental differential cross section[15] which extends in a large range of energy, we introduce the JT coupling also on the Γ_4 level. In the next section, we refer to these two situations as $\Gamma_5\otimes t_2$ interaction model or $(\Gamma_5+\Gamma_4)\otimes t_2$ interaction model, respectively.

In both cases a suitable total number N of vibrational quanta has been chosen by looking at the stability of the eigenstates as regards N. We have required a relative energy difference of 0.01% going from N to $N+1$. Of course N depends on the strength of the JT coupling and in our calculations the maximum number of phonon needed has been $N=7$.

Following the Lanczos-recursion procedure we have performed a suitable number of overrecursions so as to obtain reliable results and remove spurious eigenstates.[32,33] When necessary, we have constructed the continued fraction expansion of the ground state Green's function $G_{00}(E)$, as illustrated in the previous section.

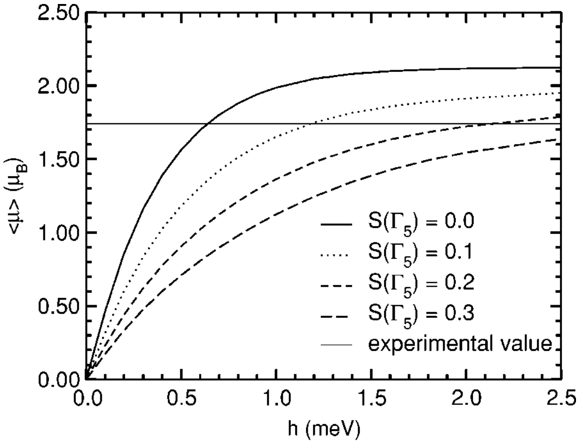

FIG. 2. Behavior of the ordered magnetic moment at $T=4.2$ K as a function of h for different values of $S(\Gamma_5)$. The other parameters are $\hbar\omega=10$ meV, $W=4.557$ meV, $x=0.875$.

A. $\Gamma_5 \otimes t_2$ interaction model

The vibronic states of U^{4+} ions are calculated considering a JT interaction only on Γ_5 level. The total Hamiltonian H_T is then

$$H_T = H_{\mathrm{CF}} + H_{magn} + H_v(\Gamma_5) + H_{\mathrm{JT}}(\Gamma_5). \tag{12}$$

The CF parameters W and x have been chosen as $W=4.557$ meV and $x=0.875$ in such a way as to reproduce the experimental energy separation among Γ_5 and Γ_3, Γ_4, and Γ_1 levels. (In meV they are, respectively, 152.4±0.2, 162.2±0.6, 173.7±0.7, 183.0±0.2.)[15] As expected, since here the CF effect plays the dominant role in determining the scale of the splittings, our values of W and x agree with the corresponding quantities given in the literature[15] without a dynamical JT coupling.

The ordered magnetic moment $\langle\mu\rangle$ has been calculated at $T=4.2$ K as a function of h for different values of strength of the coupling $S(\Gamma_5)$. The results obtained are summarized in Fig. 2, where the horizontal line corresponds to the experimental value $\langle\mu\rangle=1.74\mu_B$. Looking at this figure, for $h=0.65$ meV a right value of the ordered magnetic moment can be achieved also without JT coupling, due to the mixing of the CF levels. However, in the range of h suggested by Osborn *et al.*,[15] (in meV, $1 \leqslant h \leqslant 1.6$), a JT coupling with $0.073 \leqslant S(\Gamma_5) \leqslant 0.2$ has to be considered to reproduce the experimental value of the ordered magnetic moment. For $h=1.3$ meV, as chosen in the next $(\Gamma_5+\Gamma_4)\otimes t_2$ interaction model, the proper value of $S(\Gamma_5)$ results is 0.117. Notice that there is a competition between the effect of the local magnetic field and that of the vibronic interaction; the first one tends to increase $\langle\mu\rangle$ and the splitting of the levels, and on the contrary a larger vibronic interaction, higher $S(\Gamma_5)$, tends to approach the levels and to quench $\langle\mu\rangle$. In Table I we display some values of h and the related $S(\Gamma_5)$ values, showing evidence of a quadratic dependence of h from S. The interpolating function is $h=a+bS(\Gamma_5)+cS^2(\Gamma_5)$ with $a=0.653$, $b=3.333$, and $c=19.066$ (in meV).

TABLE I. Values of h and $S(\Gamma_5)$ giving $\langle\mu\rangle=1.74\mu_B$.

h (meV)	0.65	0.80	1.00	1.20	1.40	1.60	1.80	2.00
$S(\Gamma_5)(10^{-1})$	0.00	0.36	0.73	1.03	1.29	1.53	1.73	1.92

Then we have calculated the differential cross section. We have verified, as expected, that the experimental energy transitions and the peak intensities of the neutron spectra cannot be reproduced whatever we choose the parameters to be in the range allowed, so confirming the opportunity to consider a JT coupling also on the Γ_4 multiplet, as shown in the following section.

B. $(\Gamma_5+\Gamma_4)\otimes t_2$ interaction model

In this model a JT coupling also to the Γ_4 triplet is taken into account and in the total Hamiltonian (11) the corresponding vibrational Hamiltonian $H_v(\Gamma_4)$ and interaction Hamiltonian $H_{\mathrm{JT}}(\Gamma_4)$ are added. We have calculated the vibronic levels and the differential cross section for transitions from the lower vibronic levels (associated to the Γ_5 triplet) to excited vibronic levels in the energy range of the experimental spectrum[15] and associated also to the Γ_3 and Γ_4 CF states.

In Fig. 3 we show the spectrum calculated at $T=6.5$ K choosing $S(\Gamma_4)=0.47$; $\hbar\omega$ and $S(\Gamma_5)$ take the same values as in previous section. The values of the CF parameters have been updated ($W=4.17$ meV, $x=0.812$) to better reproduce the energy separations among the four experimental peaks. We have verified that this variation of a few percent in the CF parameters produces a variation of per thousand in the ordered magnetic moment, not significant, as, on the other hand, expected in the literature.[7]

In Fig. 4 we show the behavior of the vibronic levels at increasing $S(\Gamma_4)$ in a limited energy range around 152 meV. We also indicate the symmetry of the main zero-phonon component of the corresponding eigenstate: a circle (cross) is used when the Γ_3 (Γ_4) component dominates.

As can be seen, from Fig. 3, there are more transitions contributing to the different lines. In particular, in Fig. 4 the first line is due to transitions to excited vibronic states having

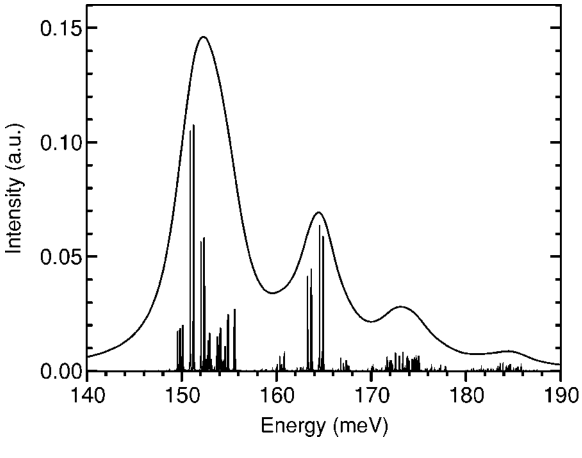

FIG. 3. Spectrum at $T=6.5$ K for $S(\Gamma_4)=0.47$, $\hbar\omega=10$ meV, $W=4.17$ meV, $x=0.812$.

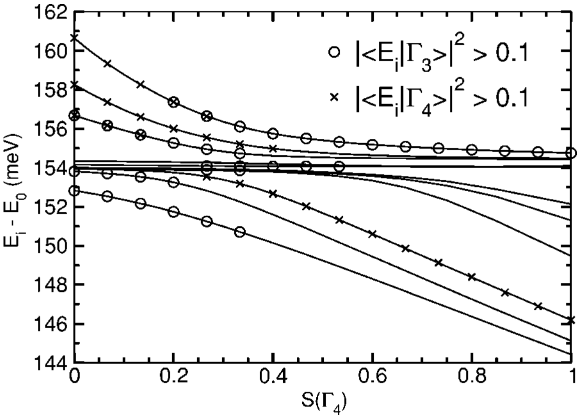

FIG. 4. Behavior of the first excited vibronic levels as a function of $S(\Gamma_4)$. The symmetry of the dominant component in the corresponding eigenstates is indicated with a circle (Γ_3) or a cross (Γ_4).

zero-phonon components of Γ_3 and Γ_4 symmetries. Moreover, for $0.4 \leqslant S(\Gamma_4) \leqslant 0.5$ the possibility of transitions separated by about 2 meV is evident. This could explain the splitting of the first band at 152 meV observed at higher temperatures, since the magnetic field alone cannot reproduce the experimental splitting of 2 meV in the accepted range for the *h* values.

V. CONCLUSIONS

We have proposed a simple microscopic model, including CF, magnetic exchange interaction, and dynamical JT coupling to a trigonal phonon mode to explain the reduction of the ordered magnetic moment and to interpret the experimental neutron spectra at low temperature. We have found that, even if weak, the JT coupling plays an essential role in giving the right value of the ordered magnetic moment and in reproducing the measured neutron spectra. In the former case we have found that it is enough to consider a JT coupling only on the ground Γ_5 triplet while in the latter a JT coupling also on the Γ_4 triplet is required. We have obtained the right value for the reduced ordered magnetic moment and a very good agreement with the measured neutron spectra.

The number of free parameters is not so large as it appears at first sight. In fact the observed interplay between the local magnetic-field interaction and JT coupling allows us to find out the strength of the JT coupling with the Γ_5 CF level once a value for *h* is chosen; on the other hand, a limited range of *h* can lead to reasonable values for the Neél temperature.[15] The energy of the phonon mode is taken fixed from the phonon branches, and the CF parameters are determined by the observed energy separation among the experimental four peaks in the neutron spectra. At the end the coupling to the Γ_4 CF state is the only true free parameter and it influences the internal splitting of the first line and the intensities of the transitions.

In light of the results obtained, we think that this simple model can be a good starting point for interpreting a larger number of experimental facts, for instance, the observed 3-**k** distortion, not in conflict with our model. The introduction of a cooperative dynamical JT effect should be the next step as a natural evolution of the model here proposed.

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

[2] S. J. Allen, Phys. Rev. **166**, 530 (1968); Phys. Rev. **167**, 492 (1968).

[3] K. Sasaki and Y. Obata, J. Phys. Soc. Jpn. **28**, 1157 (1970).

[4] S.-K. Chan and D. J. Lam, in *The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby (Academic, New York, 1974).

[5] G. Solt and P. Erdös, Phys. Rev. B **22**, 4718 (1980).

[6] P. Giannozzi and P. Erdös, J. Magn. Magn. Mater. **67**, 75 (1987).

[7] H. U. Rahman, Physica B **252**, 160 (1998).

[8] K. N. Kudin, G. E. Scuseria, and R. L. Martin, Phys. Rev. Lett. **89**, 266 402 (2002).

[9] V. S. Mironov, L. F. Chibotaru, and A. Ceulemans, Adv. Quantum Chem. **44**, 599 (2003).

[10] R. Laskowski, G. K. H. Madsen, P. Blaha, and K. Schwarz, Phys. Rev. B **69**, 140408(R) (2004).

[11] B. C. Frazer, G. Shirane, D. E. Cox, and C. E. Olsen, Phys. Rev. **140**, 1448 (1965).

[12] G. Dolling, R. A. Cowley, and A. D. B. Woods, Can. J. Phys. **43**, 1397 (1965); G. Dolling and R. A. Cowley, Phys. Rev. Lett. **16**, 683 (1966); R. A. Cowley and G. Dolling, Phys. Rev. **167**, 464 (1968).

[13] J. Faber, G. H. Lander, and B. R. Cooper, Phys. Rev. Lett. **35**, 1770 (1975); J. Faber and G. H. Lander, Phys. Rev. B **14**, 1151 (1976).

[14] P. Burlet, J. Rossat-Mignod, S. Quezel, O. Vogt, J. C. Spirlet, and J. Rebizant, J. Less-Common Met. **121**, 121 (1986).

[15] R. Osborn, A. D. Taylor, Z. A. Bowden, M. A. Hackett, W. Hayes, M. T. Hutchings, G. Amoretti, R. Caciuffo, A. Blaise, and J. M. Fournier, J. Phys. C **21**, L931 (1988); G. Amoretti, A. Blaise, R. Caciuffo, J. M. Fournier, M. T. Hutchings, R. Osborn, and A. D. Taylor, Phys. Rev. B **40**, 1856 (1989).

[16] G. Amoretti, R. Caciuffo, P. Santini, G. H. Lander, J. Kulda, and P. de V. Du Plessis, J. Appl. Phys. **85**, 4524 (1999); R. Caciuffo, G. Amoretti, P. Santini, G. H. Lander, J. Kulda, and P. de V. Du Plessis, Phys. Rev. B **59**, 13 892 (1999).

[17] K. Ikushima, S. Tsutsui, Y. Haga, H. Yasuoka, R. E. Walstedt, N. M. Masaki, A. Nakamura, S. Nasu and Y. Onuski, Phys. Rev. B **63**, 104 404 (2001).

[18] D. Kolberg, F. Wastin, J. Rebizant, P. Boulet, G. H. Lander, and J. Schoenes, Phys. Rev. B **66**, 214 418 (2002).

[19] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT University Press, Cambridge, MA, 1963).

[20] C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 255 (1950); **49**, 33 (1952); *Applied Analysis* (Prentice-Hall, Englewood Cliffs, NJ, 1956).

[21] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **5**, 2845 (1972); **8**, 2591 (1975); see also D. W. Bullet, R. Haydock, and

M. J. Kelly, in *Solid State Physics*, edited by H. Erhenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35.

[22] G. Grosso and G. Pastori Parravicini, Adv. Chem. Phys. **62**, 81 (1985); **62**, 133 (1985).

[23] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[24] I. B. Bersuker and V. Z. Polinger, in *Vibronic Interactions in Molecules and Crystals*, Springer Series in Chemical Physics (Springer-Verlag, Berlin, 1989).

[25] G. Bevilacqua, L. Martinelli, and G. Pastori Parravicini, J. Phys.: Condens. Matter **10**, 10 347 (1998).

[26] M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1967), Vol. 20.

[27] G. Bevilacqua, D. Ippolito, and L. Martinelli, Phys. Rev. B **69**, 155 208 (2004).

[28] G. Grosso and G. Pastori Parravicini, *Solid State Physics* (Academic Press, London, 2000), p. 185 and references therein.

[29] O. Mualin, E. E. Vogel, M. A. de Orúe, L. Martinelli, G. Bevilacqua, and H.-J. Schulz, Phys. Rev. B **65**, 035 211 (2001); G. Bevilacqua, L. Martinelli, and E. E. Vogel, Phys. Rev. B **66**, 155 338 (2002).

[30] W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Oxford University Press, Oxford, U.K., 1971); S. W. Lovesey, *Theory of Thermal Neutron Scattering from Condensed Matter* (Oxford University Press, Oxford, U.K., 1884).

[31] D. Ippolito, Thesis, University of Pisa, 2002.

[32] J. C. Cullum and R. A. Willoughby, *Lanczsos Algorithms for Large Symmetric Eigenvalue Computations* (Birkhauser, Boston, 1985), Vols. I and II.

[33] L. Martinelli, G. Bevilacqua, J. Rivera-Iratchet, M. A. de Orue, O. Mualin, E. E. Vogel, and J. Cartes, Phys. Rev. B **62** 10 873 (2000).