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Perturbative approach to *J* mixing in *f*-electron systems: Application to actinide dioxides

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We present a perturbative model for crystal-field calculations, which keeps into account the possible mixing of states labelled by different quantum number *J*. Analytical *J*-mixing results are obtained for a Hamiltonian of cubic symmetry and used to interpret published experimental data for actinide dioxides. A unified picture for all the considered compounds is proposed by taking into account the scaling properties of the crystal-field potential.

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I. INTRODUCTION

Crystal-field (CF) theory[1] is one of the most powerful theoretical methods to deal with the magnetic properties of rare-earth (RE) and actinide (An) ions, and Stevens' operator equivalents formalism is still the most commonly used to analyze experimental data due to its simplicity. Unfortunately, this approach concentrates only on the CF splittings within the lowest-lying $^{2S+1}L_J$ multiplet of the considered ion, completely neglecting the contributions of excited multiplets ("*J* mixing"). Although the task of diagonalizing the large matrices related to the full f^n configuration, including different *J* multiplets, is relatively easy to perform numerically by means of today's computers, Stevens' approach often makes it possible to obtain analytical expressions for physical quantities of interest for systems of sufficiently high symmetry, thus leading to a deeper insight on the physics of several compounds.

In the present paper, we discuss a perturbative approach which retains the validity of Stevens' formalism while correctly taking into account *J*-mixing effects. This method, which has led to interesting results for transition-metal (TM) based molecular clusters[2,3] and ferromagnetic exchange-driven RE-TM intermetallic compounds[4] is now applied to evaluate the intramultiplet CF splittings in light An and RE ions. We exploit the method to analyze the CF of actinide dioxides. These large-gap semiconductors are among the most studied actinide compounds. Although *f*-electrons are well localized, the complexity of the magnetic Hamiltonian, which includes CF and magnetoelastic single-ion interactions, phonon-transmitted quadrupolar interactions, and multipolar superexchange couplings between neighboring ions, leads to a number of interesting and unusual physical phenomena. Among them, we mention the proposed octupolar phase transition in NpO_2,[5,6] the observed CF-phonon bound states in NpO_2,[7] and the peculiar static and dynamic phenomena produced by magnetoelastic interactions in UO_2,[8–10] some of which are not yet fully understood.

The CF potential is the fundamental building block of any theoretical model of the properties of dioxides, since this influences the single-ion behavior to a large extent. In particular, it determines which degrees of freedom of the *f* shell are left unquenched and the size of the corresponding multipole moments, which account for the low-*T* physical properties. Most of the published theoretical approaches are based on the above-mentioned Stevens' treatment of the CF, which includes only the lowest Russell-Saunders or intermediate-coupling multiplet of the ion. If one takes as starting point the CF of UO_2, on which very detailed information is available by inelastic neutron scattering (INS) experiments,[11] then scaling the CF of UO_2 within the Stevens' framework (to take into account the different ionic radii) provides a good CF model for NpO_2. However, the same scheme applied to PuO_2 is only qualitatively satisfactory, since it reproduces the correct level sequence but it underestimates the observed energy splitting.

Moreover, this approach is not internally consistent because the so-obtained CF parameters yield different results when additional ionic multiplets are included in the calculation. On the other hand, the increased complexity of *J* mixing calculations makes particularly hard to find CF parameter sets working consistently over the various compounds. Indeed, different sets have been proposed so far for dioxides within *J* mixing calculations. In particular, in NpO_2 two distinct and equally good sets of parameters had been obtained.[12]

By our perturbative *J* mixing approach, we have been able to obtain a unique set which works well over all the considered compounds.

II. THE PERTURBATIVE *J*-MIXING MODEL

Following Ref. 13, the total free-ion (FI) and crystal-field (CF) Hamiltonian $H=H_{\mathrm{FI}}+H_{\mathrm{CF}}$, with

$$H_{\mathrm{CF}} = \sum_{k,q} B_k^q C_q^{(k)} \tag{1}$$

can be rewritten in the form

$$H = H_0 + H_1 + H_2, \tag{2}$$

where in the present case H_0 coincides with H_{FI} and H_1 and H_2 are chosen so that the former has nonzero matrix elements only between states belonging to the same ${}^{2S+1}L_J$ multiplet. It is possible to define a Hermitian operator Ω such that the matrix element of the transformed Hamiltonian $H'=e^{-i\Omega}He^{i\Omega}$ are very small in the off-diagonal blocks, thus restoring the possibility to use an isolated-multiplet approach. In this framework,[13]

$$\langle \alpha JM|H'|\alpha JM'\rangle = E_{0\alpha J}\delta_{MM'} + \langle \alpha JM|H_1|\alpha JM'\rangle - \sum_{\alpha''J''M''} \frac{\langle \alpha JM|H_2|\alpha''J''M''\rangle\langle \alpha''J''M''|H_2|\alpha JM'\rangle}{E_{0\alpha''J''} - E_{0\alpha J}}, \tag{3}$$

where α, J label free ion manifolds and $E_{0\alpha J}$ are the eigenvalues of H_0. For clarity, in the following we will label the states as in the Russell-Saunders scheme, where α coincides with (L,S) and any additional quantum number necessary to identify the terms; yet the actual calculation will include intermediate-coupling corrections to the eigenfunctions.

Once we limit our calculations to the ground J multiplet only, the first term on the right-hand side of the above equation represents a uniform energy shift of the whole multiplet, while the second term is the usual ground-multiplet CF Hamiltonian $H^{(J)}$. The effect of J-mixing is accounted for by the third term, which will be considered as an extra contribution to the ground-multiplet Hamiltonian and labelled $H_{\text{mix}}^{(J)}$ [we maintain the redundant superscript (J) notation in order to emphasize that the newly obtained J-mixing Hamiltonian *also* acts on the ground multiplet *only*].

In the case of light actinides, the most important J-mixing contribution comes from the two lowest J-multiplets, i.e., ${}^{2S+1}L_J$ and ${}^{2S+1}L_{J+1}$. Therefore, for the sake of simplicity we restrict our analysis to the case of these two multiplets, separated by an energy gap Δ by the spin-orbit interaction. From Eq. (3), $H_{\text{mix}}^{(J)}$ can be written as

$$\langle JM|H_{\text{mix}}^{(J)}|JM'\rangle = -\sum_{M''}\sum_{k,q}\sum_{k',q'} B_k^q B_{k'}^{q'} \times \frac{\langle JM|C_q^{(k)}|J+1M''\rangle\langle J+1M''|C_{q'}^{(k')}|JM'\rangle}{\Delta}. \tag{4}$$

The Wigner-Eckart theorem, in the form

$$\langle J_1M_1|C_q^{(k)}|J_2M_2\rangle = (-1)^{J_1-M_1}\langle J_1\|C^{(k)}\|J_2\rangle \begin{pmatrix} J_1 & k & J_2 \\ -M_1 & q & M_2 \end{pmatrix} \tag{5}$$

allows us to get rid of the sum over M'' in Eq. (4), since the $3j$ symbol in Eq. (5) equals zero if $M_2 \neq M_1 - q$. The products of $3j$ symbols can be rewritten as linear combinations of matrix elements of Stevens operators O_k^q,[2,4] so that

$$H_{\text{mix}}^{(J)} = \sum_{k,q,k',q'} \frac{B_k^q B_{k'}^{q'}}{\Delta} M_{k+k'}^{q+q'}, \tag{6}$$

where the "mixing operators" M_n^m are[2]

$$M_n^m = \sum_{p=0}^{n} c_{n,p}^{(m)} O_p^m \tag{7}$$

with conveniently defined $c_{n,p}^{(m)}$ coefficients.

Let us consider the simple but important case of cubic symmetry, for which the CF Hamiltonian (1) has the form

$$H_{\text{CF}} = B_4^0\Big[C_0^{(4)} + \sqrt{\tfrac{5}{14}}(C_4^{(4)} + C_{-4}^{(4)})\Big] + B_6^0\Big[C_0^{(6)} - \sqrt{\tfrac{7}{2}}(C_4^{(6)} + C_{-4}^{(6)})\Big]. \tag{8}$$

Restricting the calculations within the ground multiplet only and using the Stevens' operator equivalents formalism, Eq. (8) becomes

$$H_{\text{CF}}^{(J)} = \frac{B_4^0}{8}\beta(O_4^0 + 5O_4^4) + \frac{B_6^0}{16}\gamma(O_6^0 - 21O_6^4), \tag{9}$$

β and γ being the fourth- and sixth-order Stevens factors. To introduce another common notation,[1] we define

$$V_4 = \frac{B_4^0}{8} = A_4\langle r^4\rangle, \quad V_6 = \frac{B_6^0}{16} = A_6\langle r^6\rangle, \tag{10}$$

where $\langle r^n\rangle$ are the expectation values of the r^n operator over the appropriate f-electron wave function. It is found that $H_{\text{mix}}^{(J)}$ maintains the cubic symmetry, and has the form

$$H_{\text{mix}}^{(J)} = \nu_4(O_4^0 + 5O_4^4) + \nu_6(O_6^0 - 21O_6^4) + \nu_8(O_8^0 + 28O_8^4 + 65O_8^8) + \cdots, \tag{11}$$

where we did not explicitly write the terms containing operators of rank higher than 8 since $O_k^q=0$ for $k>2J$, and $J=9/2$ is the maximum possible value for the ground state of light lanthanides and actinides.[14] The coefficients appearing in Eq. (11) are dependent on J and can be written as

$$\nu_k = \frac{1}{\Delta}[\nu_k^{(4,4)}(V_4\langle J\|C^{(4)}\|J+1\rangle)^2 + \nu_k^{(6,6)}(V_6\langle J\|C^{(6)}\|J+1\rangle)^2 + \nu_k^{(4,6)}(V_4\langle J\|C^{(4)}\|J+1\rangle V_6\langle J\|C^{(6)}\|J+1\rangle)], \tag{12}$$

and a list of $\nu_k^{(m,n)}$ for the ground multiplets of f^n configurations with $1\leqslant n\leqslant 5$ is given in Table I. The reduced matrix elements $\langle J\|C^{(k)}\|J+1\rangle$ are calculated by using the intermediate-coupling free-ion wave functions.

Ions with six f electrons have a $J=0$ ground singlet, so that no intramultiplet energy splitting can exist and J-mixing effects are evident only in the wave function composition;

TABLE I. $\nu_k^{(m,n)}(J)$ coefficients for values of J corresponding to the ground state of light lanthanides and actinides.

Coefficient	$J=5/2$	$J=4$	$J=9/2$
$\nu_4^{(4,4)}$	$32/10395$	$-1328/2760615$	$-296/920205$
$\nu_4^{(6,6)}$	$64/(33\sqrt{455})$	$-\sqrt{2/35}\times 256/184041$	$-\sqrt{17/7}\times 128/184041$
$\nu_4^{(4,6)}$	$448/6435$	$-6464/920205$	$-39488/15643485$
$\nu_6^{(4,4)}$	0	$-1928/93648555$	$-452/52026975$
$\nu_6^{(6,6)}$	0	$-\sqrt{2/35}\times 32/212355$	$4/(212355\sqrt{119})$
$\nu_6^{(4,6)}$	0	$-512/22297275$	$-1072/126351225$
$\nu_8^{(4,4)}$	0	$2/36891855$	$4/184459275$
$\nu_8^{(6,6)}$	0	$-\sqrt{2/35}\times 2/250965$	$-1/(150579\sqrt{119})$
$\nu_8^{(4.6)}$	0	$7/418275$	$49/14221350$

this case is then impossible to study by the present approach. As for ions with half-filled f shell such as Gd^{3+}, Cm^{3+}, and Bk^{4+}, J mixing is generally negligible and it hardly affects any physical property. Finally, the perturbative J-mixing approach is in principle suitable to study heavy f-electron ions ($8 \leqslant n \leqslant 13$), taking into account that the ground J multiplet is mixed with $J-1$ states, instead of $J+1$. However, in this case the advantage of using the perturbative model with respect to the numerical diagonalization of H over a complete f^n basis could be significantly reduced, because (i) the use of Stevens operators of rank 10 (12) becomes necessary for $J \geqslant 5$ (6); (ii) it is not always possible to diagonalize $H_{\mathrm{CF}}^{(J)} + H_{\mathrm{mix}}^{(J)}$ analytically, even in cubic symmetry. In any case, the expected J-mixing strength is much smaller for heavy than for light elements.

III. A PARTICULAR CASE: THE f^1 CONFIGURATION

In order to show in detail how the present model can be applied to the study of rare-earth and actinide compounds, let us start from the simplest possible configuration, an ion with a single f electron. The only interaction present in the free-ion Hamiltonian is the spin-orbit coupling,

$$H_{\mathrm{FI}} = \Lambda \mathbf{L} \cdot \mathbf{S}. \tag{13}$$

The f^1 spectra is composed of two multiplets only, ${}^2F_{5/2}$ (ground state) and ${}^2F_{7/2}$; adding a crystal field of cubic symmetry, the 14×14 matrix representing the ${}^2F$ term is made up of two 4×4 and two 3×3 diagonal blocks. The complete Hamiltonian H can then be analytically diagonalized, and the resulting energy gap between the Γ_7 doublet and a Γ_8 quartet composing the ground multiplet is

$$\begin{aligned} E_{\Gamma_7} - E_{\Gamma_8} = \tfrac{1}{1716}\Big[&3744V_4 - 4480V_6 + \sqrt{25600(13V_4 - 84V_6)^2 - 137280(13V_4 - 84V_6)\Lambda + 9018009\Lambda^2} \\ &- \sqrt{16384(13V_4 + 70V_6)^2 - 219648(13V_4 + 70V_6)\Lambda + 9018009\Lambda^2}\Big]. \end{aligned} \tag{14}$$

Although the perturbative approach is not particularly useful here since an exact analytical solution can be obtained, let us study this simple case in order to clarify the details of the process and to understand its limits of validity. No intermediate coupling occurs, and $\beta = 2/315$, $\gamma = 0$, $\langle J \| C^4 \| J+1 \rangle = 2\sqrt{10/77}$, and $\langle J \| C^6 \| J+1 \rangle = -10\sqrt{2/143}$; moreover, the spin-orbit gap can be expressed as $\Delta = \Lambda(J+1) = 7\Lambda/2$, with $\Lambda = 100.5$ meV. Diagonalizing $H_{\mathrm{CF}}^{(J)} + H_{\mathrm{mix}}^{(J)}$ (see Appendix for details), we find

$$\begin{aligned} E_{\Gamma_7} - E_{\Gamma_8} = \frac{16}{7}V_4 + \frac{1}{\Lambda}\bigg(&\frac{20480}{124509}V_4^2 - \frac{614400}{77077}V_4V_6 \\ &+ \frac{204800}{20449}V_6^2\bigg), \end{aligned} \tag{15}$$

which corresponds exactly to the series expansion of Eq. (14) up to the first order in Λ^{-1}.

The intramultiplet energy gap calculated above can be directly measured by means of spectroscopic techniques; for

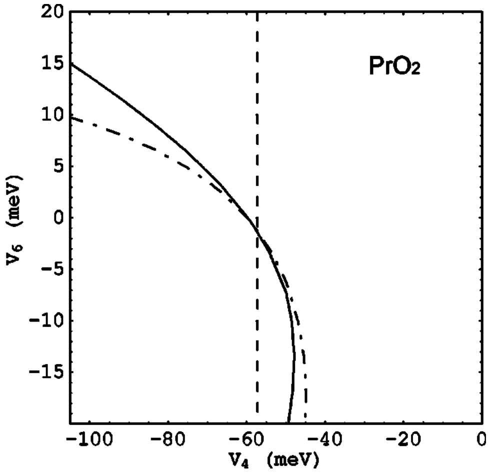

FIG. 1. Possible solutions of the equation $E_{\Gamma_7}-E_{\Gamma_8}=131$ meV in terms of the crystal-field parameters V_4 and V_6 of PrO_2. Full line, J-mixing effects are taken into account by exact diagonalization of the full f^1 Hamiltonian [Eq. (14)]. Dashed line, J-mixing effects are neglected. Dashed-dotted line, J-mixing effects are taken into account perturbatively [Eq. (15)].

example, inelastic neutron scattering measurements for PrO_2 (where praseodymium ions have valence 4+, therefore presenting a $4f^1$ electronic configuration) have shown that $E_{\Gamma_7}-E_{\Gamma_8}=131$ meV.[15] Figure 1 shows the possible solutions of this equation in terms of the crystal-field parameters V_4 and V_6, with three different expressions: the full black line corresponds to the exact diagonalization of the complete f^1 Hamiltonian [Eq. (14)]; the dashed vertical line is obtained by neglecting J mixing and using Stevens' approximation $E_{\Gamma_7}-E_{\Gamma_8}=(16/7)V_4$; finally, the dashed-dotted line takes J mixing into account perturbatively by the present approach [Eq. (15)]. The results are satisfactory, the agreement between the exact (full) and approximate (dashed-dotted) curves is qualitatively much better if compared with Stevens' approximation (dashed line), and the quantitative contribution of the excited states is correctly estimated in the small-CF range $|V_k/\Lambda|<1$. It may be noticed that the three curves of Fig. 1 almost coincide when $V_6\simeq 0$, since in this case the largest part of the J-mixing correction (which is linear in V_6) vanishes [this can be verified by observing the relative magnitude of the different coefficients in Eq. (15)]. For the same reason, for small V_6, the value of V_4 is slightly underestimated for $V_6<0$ and overestimated for $V_6>0$. As the spin-orbit interaction is stronger for heavier ions and the gap between the two lowest multiplets grows with J, we expect our model to have a reasonably good performance over the whole lanthanide and actinide series.

IV. THE CUBIC PHASE OF ACTINIDE DIOXIDES

In this section, the perturbative J-mixing model outlined so far will be applied to interpret the intramultiplet crystal-field splittings observed by inelastic neutron scattering (INS) for actinide dioxides AnO_2 (An=U, Np, Pu). The crystal-field analysis will be performed in terms of the parameters A_4 and A_6 [Eq. (10)] instead of V_4 and V_6, using the values of $\langle r^n\rangle$ given in Ref. 17. Although recent density functional studies have pointed out a certain degree of covalency for the An—O bond in these systems,[16] this does not prevent one from using the crystal field theory to analyze experimental data; it would be quite more difficult than in a ionic compound to calculate the CF parameters from first principles, but this is not our aim. We will demonstrate that the present method can be used for an analytical study of the experimental results over a wide range of parameters and compositions.

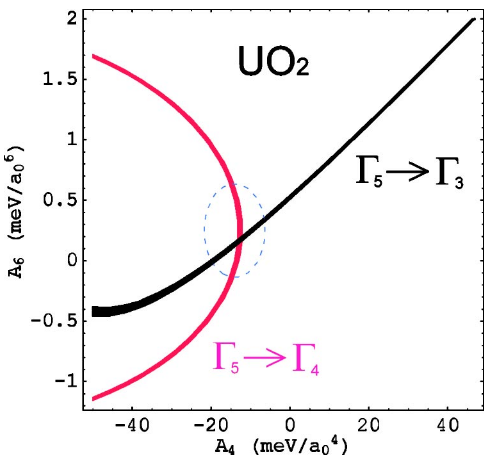

FIG. 2. (Color online) Possible solutions of the disequations $165\ \text{meV}\leqslant E_{\Gamma_4}-E_{\Gamma_5}\leqslant 179$ meV and $150\ \text{meV}\leqslant E_{\Gamma_3}-E_{\Gamma_5}\leqslant 160$ meV, in terms of the crystal-field parameters A_4 and A_6 of UO_2. The dashed ellipse represents the "safe zone" defined in the text.

INS spectra for UO_2 in the paramagnetic phase (above $T_N=30.8$ K) display peaks between 150 ad 185 meV,[11,18] which have been attributed to transitions between the Γ_5 ground state[11,18,19] and excited Γ_3 and Γ_4 states, and no other magnetic transitions were reported up to 700 meV (Ref. 11) (it is worth to recall that the $\Gamma_5\rightarrow\Gamma_1$ transition is not dipole allowed so, if present, it will display a very small intensity with respect to the other two transitions).

Figure 2 shows the values of A_4 and A_6 for which the possible transitions lie within the experimentally observed range according to the perturbative model. In the preceding section, we have studied the quantitative discrepancy between the model's predictions and the exact results, which was found to be significant for large CF parameters. Following these estimates, we have determined a "safe zone" (indicated in Fig. 2 by a dashed ellipse) within which the true set of CF parameters for UO_2 is located with high degree of confidence.

For the paramagnetic phase of NpO_2 we have followed Amoretti *et al.*,[12] who observed a broad magnetic signal centered at 55 meV in the INS spectra and attributed this peak to a transition between the two Γ_8 quartets. They gave two possible solutions for the paramagnetic phase, labelled 3 and 4 in Fig. 3; we show that actually there are infinite possible solutions, divided in two branches.

PuO_2 displays a temperature-independent magnetic susceptibility below 1000 K,[20] so that the CF ground state is expected to be the Γ_1 singlet. Magnetic-dipole matrix elements involving this state within the $^5I_4$ multiplet are zero

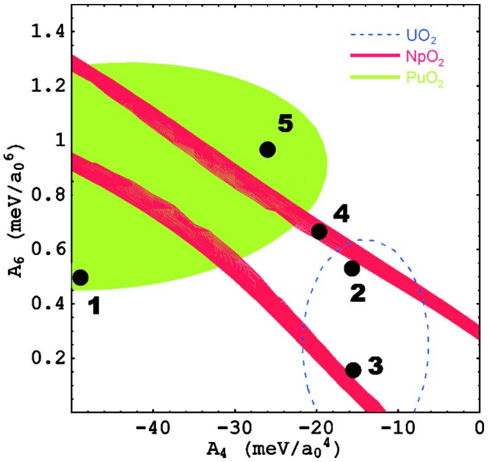

FIG. 3. (Color online) Possible solutions of the equations $E_{\Gamma_8^{(1)}} - E_{\Gamma_8^{(2)}} = 55 \pm 5$ meV (NpO$_2$), $E_{\Gamma_4} - E_{\Gamma_1} = 123 \pm 5$ meV (PuO$_2$), in terms of the crystal-field parameters A_4 and A_6. The dashed ellipse near the bottom-right corner represents the "safe zone" for UO$_2$ (see Fig. 2); the numbered dots are sets of parameters found in the literature for different compounds (see Table II for details).

except with the Γ_4 triplet. Indeed, only one peak centered at 123 meV is observed in PuO$_2$ INS spectra.[21] According to our perturbative model there are again infinite possible solutions, plotted in Fig. 3, which cover a large area of the A_4-vs-A_6 diagram.

It is clear that, in the case of AnO$_2$, the INS data analysis cannot give unambiguous results if every compound is treated separately; this can also be inferred from the widely scattered sets of parameters which are found in the literature (some of which are listed in Table II and displayed in Fig. 3). On the other hand, if we assume that the A_k parameters are approximately the same for all isostructural compounds,[1] an inspection of Fig. 3 shows that the only area of the diagram where common solutions for An=U, Np, Pu might exist is around the point labelled 4, which corresponds to one of the two solutions (the "strong *J*-mixing" one) proposed by Amoretti *et al.*[12] for NpO$_2$ ($A_4 = -19.6$ meV/a_0^4; $A_6 = 0.666$ meV/a_0^6). In order to verify this result, we have calculated the INS transition energies for UO$_2$, NpO$_2$, PuO$_2$, and PrO$_2$ with this set of parameters by numerical diagonalization of the complete f^n configuration Hamiltonian (Table III). Moreover, as a further test, we have calculated the magnetic susceptibility for AmO$_2$ and CfO$_2$ with the same parameters (Fig. 4; the measurements can be found in Refs. 22 and 23, respectively).

TABLE II. Crystal-field parameters found in the literature for various actinide dioxides. The labels correspond to those used in Fig. 3.

Label	Compound	V_4 (meV)	V_6 (meV)	Source
1	UO$_2$	−409	24.8	Ref. 19
2	UO$_2$	−123	26.5	Ref. 11
3	NpO$_2$	−104	6.2	Ref. 12
4	NpO$_2$	−132	26.4	Ref. 12
5	PuO$_2$	−151	31.0	Ref. 21

TABLE III. The intramultiplet transition energies experimentally detected by INS for some actinide and rare-earth dioxides are compared with the corresponding energy splitting calculated in a *J*-mixing framework with the unique set of parameters $A_4 = -19.6$ meV/a_0^4, $A_6 = 0.666$ meV/a_0^6 (i.e., the solution labelled 4 in Fig. 3).

		Energy (meV)	
Compound	Transition	Expt. (meV)	Calc.(meV)
UO$_2$	$\Gamma_5 \rightarrow \Gamma_3$	155[a]	167
UO$_2$	$\Gamma_5 \rightarrow \Gamma_4$	172[a]	187
NpO$_2$	$\Gamma_8^{(2)} \rightarrow \Gamma_8^{(1)}$	55[b]	56
PuO$_2$	$\Gamma_1 \rightarrow \Gamma_4$	123[c]	112
PrO$_2$	$\Gamma_8 \rightarrow \Gamma_7$	131[d]	82

[a] References 11 and 18.
[b] Reference 12.
[c] Reference 21.
[d] Reference 15.

In all the cases examined so far, the comparison with experimental results is quite good, considering that a 100% exact scaling of the CF potential is not expected to hold. Therefore, our results point towards a coherent unified picture for the CF potential in actinide dioxides.

The splitting predicted for PrO$_2$ seems less satisfactory as the measured value of the gap $E(\Gamma_7) - E(\Gamma_8) = 131$ meV is quite larger than the value calculated with the solution we propose. However, the PrO$_2$ case is complicated by magnetoelastic interactions that are known to affect heavily the physics of this compound by increasing the bare value of the CF gap.[15] Hence, a value of this bare gap of the order of 80 meV is fully realistic.

One feature which cannot be accounted for by the CF models proposed so far is the temperature independence of the magnetic susceptibility of PuO$_2$ above 600 K. Indeed, it is obvious that if there is a magnetic gap of 123 meV as

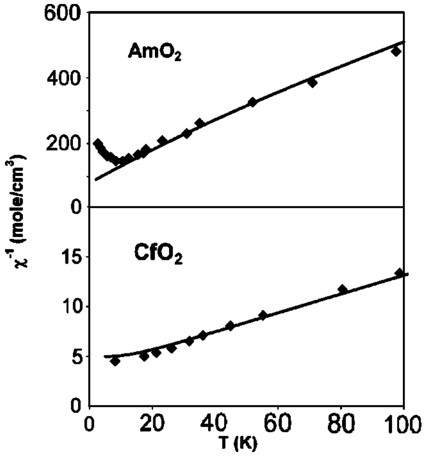

FIG. 4. Experimental (dots, Refs. 22 and 23) and calculated (lines, present work) inverse magnetic susceptibility for AmO$_2$ and CfO$_2$, with $A_4 = -19.6$ meV/a_0^4, $A_6 = 0.666$ meV/a_0^6, $\chi_{\mathrm{Am}}^{-1}(0) = 80$ mol/cm^3, $\chi_{\mathrm{Cf}}^{-1}(0) = 3$mol/cm^3.

observed by neutron scattering, when this level becomes thermally populated it will contribute to the susceptibility, no matter the mechanism which generates the splitting (unless this contribution is accidentally canceled by other contributions). Indeed, even a completely different approach based on density-functional-theory calculations cannot remove the discrepancy between magnetic susceptibility and neutron scattering experiments.[24] Using the diagram in Fig. 3 as a guide we have been able to find a solution for PuO$_2$ ($A_4 = -26.7\ \mathrm{meV}/a_0^4$, $A_6 = 1.68\ \mathrm{meV}/a_0^6$) which leads to $E_{\Gamma_4} - E_{\Gamma_1} = 134$ meV and a flat $\chi(T)$ curve below 1000 K. For this set the Curie contribution of the excited triplet and the off-diagonal Van Vleck contribution of the $\Gamma_1 - \Gamma_4$ pair accidentally combine into an almost T-independent susceptibility. However, this solution is quite unstable even for small variation of the CF parameters; moreover, it does not give good results if applied to UO$_2$ and NpO$_2$.

V. CONCLUSIONS

We have developed a perturbative approach to J mixing which allows the Stevens' formalism to be recovered by replacing the original CF Hamiltonian with an effective one operating within the same J multiplet. We have applied the method to the study of the CF in actinide dioxides. These compounds have extremely interesting physical properties, which are determined by the CF to a large extent. It is therefore important to reach a precise understanding of the CF, which is the basic building block of all theoretical efforts devoted to understand these properties. Most studies of the CF potential rely on the Stevens' approach, which yields a solution working fairly consistently over several compounds. Yet, this solution does not work satisfactorily anymore when J mixing is included, and the practical impossibility to perform exact J-mixing calculations in wide ranges of the parameter space has prevented so far the identification of a better alternative. By hugely decreasing the numerical effort in favor of analytical calculations, our method has allowed us to find a J-mixing solution ($A_4 = -19.6\ \mathrm{meV}/a_0^4$, $A_6 = 0.666\ \mathrm{meV}/a_0^6$) which works consistently over all the considered compounds.

Although in the present paper we have only studied cubic systems and included the two lowest multiplets only (which in dioxides account for almost 100% of J mixing), the method can be used for any point symmetry, at the price of additional terms in the effective Hamiltonian; also, as many multiplets as necessary can be included in the calculation, leading to additional contributions to the ν_k coefficients of Eq. (12). Even in this case our method, by allowing to perform a quantitative analysis of experimental data by means of a Stevens-type Hamiltonian containing higher-rank operators, is much more efficient than full numerical diagonalization. In particular, wide ranges of the parameter space can be easily investigated, allowing to produce quite easily diagrams such as Figs. 2 and 3 which would otherwise be very hard (if not impossible, in some cases) to obtain.

APPENDIX: ANALYTICAL DIAGONALIZATION OF A CUBIC CRYSTAL-FIELD HAMILTONIAN

This Appendix will be devoted to illustrate the results of analytical diagonalization of the cubic crystal-field Hamiltonian,

$$H^{(J)}_{\mathrm{cubic}} = \frac{b_4}{8}(O_4^0 + 5O_4^4) + \frac{b_6}{16}(O_6^0 - 21O_6^4) + \frac{b_8}{128}(O_8^0 + 28O_8^4 + 65O_8^8), \tag{A1}$$

which corresponds to $H^{(J)}_{\mathrm{CF}} + H^{(J)}_{\mathrm{mix}}$ discussed in this paper [Eqs. (9) and (11)] with $b_4 = 8V_4\beta + \nu_4$, $b_6 = 16V_6\gamma + \nu_6$, $b_8 = \nu_8$.

For $J = 5/2$ (Ce^{3+}, Pr^{4+}, Sm^{3+}, Am^{4+}, Pu^{3+}, etc.) b_6 and b_8 have no effects, and the multiplet splits in a Γ_7 doublet and a Γ_8 quartet separated by $E_{\Gamma_8} - E_{\Gamma_7} = 45b_4$.

A $J = 4$ ground multiplet (Pr^{3+}, U^{4+}, Np^{3+}, Pu^{4+}, etc.) is split into a singlet (Γ_1), a doublet (Γ_3), and two triplets (Γ_4 and Γ_5) by a cubic crystal field. The energy separations between these levels are

$$E_{\Gamma_3} - E_{\Gamma_1} = 180(-b_4 + 63b_6 - 21b_8), \tag{A2}$$

$$E_{\Gamma_4} - E_{\Gamma_1} = 105(-b_4 + 63b_6 - 216b_8), \tag{A3}$$

$$E_{\Gamma_5} - E_{\Gamma_1} = 45(-9b_4 + 105b_6 - 280b_8\ . \tag{A4}$$

For $J = 9/2$ (Nd^{3+}, Np^{4+}, U^{3+}, etc.) the multiplet splits into a Γ_7 doublet and two Γ_8 quartets, respectively, split by

$$E_{\Gamma_8^{(2)}} - E_{\Gamma_8^{(1)}} = 15\sqrt{7(103b_4^2 + 4704b_4b_6 + 85680b_6^2 - 10584b_4b_8 + 362880b_6b_8 + 3129840b_8^2)} \tag{A5}$$

and

$$E_{\Gamma_7} - E_{\Gamma_8^{(1)}} = \frac{735}{2}b_4 - 12600b_6 + 28350b_8 + \frac{(E_{\Gamma_8^{(2)}} - E_{\Gamma_8^{(1)}})}{2}. \tag{A6}$$

The above results, with their algebraical signs, are correct for any particular order of the energy levels.

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