Status of understanding of the hybridization-mediated anisotropic magnetic behavior of PuSb

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(Received 13 January 1986)

In our previous work a successful theory was developed, on the basis of hybridization-mediated anisotropic interactions, for the unusual magnetic properties of PuSb. The phase transitions and variation of ordered moment size with temperature for PuSb were explained. Calculated energies and dispersion shapes of magnetic excitations from that theory agree very well with subsequent experiments. However, there are remaining significant discrepancies between theory and experiment for the excitation behavior, and these are addressed in the present paper. Motivation for, and consequences of, including a weak quadrupole interaction are presented. Inadequacies of our earlier approximation for the intermediate-coupled ground state of $Pu^{3+}(f^5)$ are discussed, and the need to use the exact intermediate-coupled ground state is demonstrated. We also discuss the choice of selection rule used to pick out the scattering processes used to calculate the scattering amplitudes which determine the angular dependence of the anisotropic interaction between a pair of Pu^{3+} ions.

I. INTRODUCTION

Remarkable success has been achieved in recent years in understanding the unusual magnetic properties of a class of cerium and light-actinide intermetallic compounds on the basis of hybridization between moderately delocalized f electrons and band electrons.[1-5] The magnetic behavior of the heavier monopnictides of cerium and the light actinides is characterized by extremely large anisotropy with magnetic moments aligned along the cube edge. Of central interest are the large number of phase transitions (between phases with different magnetic structures) and the unusual magnetic excitations observed in the cerium compounds. These unusual features of the cerium compounds have been explained on the basis of the work of Siemann and Cooper[1] and Cooper *et al.*,[2] who extended the idea of a hybridization-mediated anisotropic two-ion interaction, first developed by Coqblin and Schrieffer[6] for dilute cerium alloys. Subsequent further extension of the theory[3-5] to the monopnictides of the light actinides (in which the actinide ion has more than one f electron) met with similar success in explaining the main features of the anisotropic magnetic equilibrium and excitation behavior, especially the unusual magnetic phase-transition behavior. Important predictive success was also achieved for the anisotropic excitation behavior. However, discrepancies remain between the theoretical predictions and experimental observations, more significantly for the excitation behavior,[7] and it is these that we will address in this paper.

The theory has successfully explained[3-5] the unusually large cube-edge anisotropy as well as the unusual transitions between phases with different magnetic structures in the monopnictides of the light actinides, particularly in[5] PuSb. One discrepancy remains between the calculated and observed equilibrium behavior. While the experimentally observed antiferromagnetic phase of PuSb (characterized by a modulation vector parallel to a cube edge, defining a direction which will henceforth be referred to as the z direction) is found to be longitudinally polarized (with moments parallel to the modulation vector), our theory predicts an antiferromagnetic phase with transverse polarization (moments along a cube edge perpendicular to the modulation vector). The same effect shows up in another related calculation. Namely, calculations[8] using this model within the random-phase approximation (RPA) have failed to find a divergence in the susceptibility of paramagnetic PuSb at the required wave vector (corresponding to the long-period antiferromagnetic ordering) when the wave vector is parallel to the moment, but do give a divergence for wave vector transverse to the moment.

Predictive calculations[5] of the energies and dispersion shapes of the magnetic excitations in PuSb (see Fig. 1) have turned out to be in excellent agreement with the results of subsequent inelastic neutron scattering experiments.[7] However, two significant discrepancies exist between the predictive calculations of the magnetic excitations in PuSb and the subsequent experimental measurements.[7] The transverse mode (lowest of three transverse modes) that coincides so well with the experimental results is not the mode that was predicted to have the greatest intensity. The transverse mode next higher in energy (with a slightly higher energy) is the one that was predicted to have the greater intensity.[5] Also, when the wave vector of the excitations is perpendicular to the magnetic moment, the experiments identify two modes near the zone boundary; while the present model predicts only one intense mode. (Each of the theoretical modes is doubly degenerate, corresponding to energy gain and energy loss.)

Of the discrepancies between theory and experiment for both equilibrium and excitation behavior, we believe the last mentioned is the least significant, since the splitting of the intensity (near the zone boundary) might arise from some weak interaction which has not been included in our calculations. The other three discrepancies may be related in that they may arise from the same "deficiency" in the

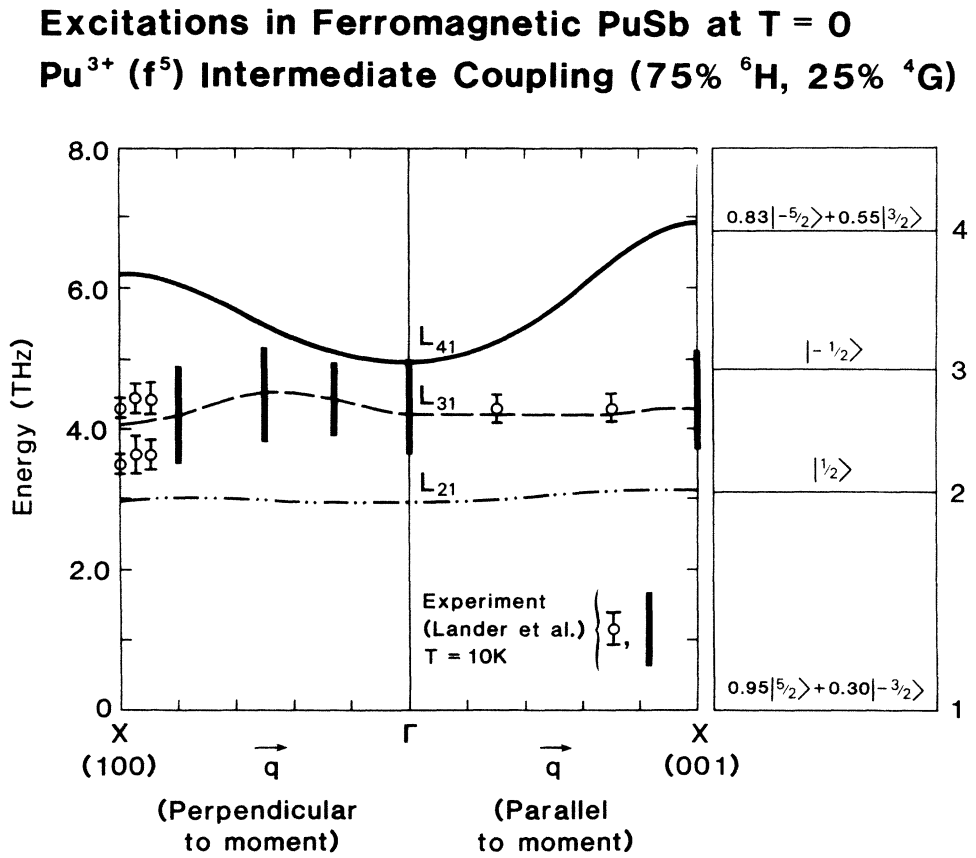

FIG. 1. Magnetic excitations in ferromagnetic PuSb. The theoretical curves reproduce the three lowest modes from Fig. 6 of Ref. 5. These were calculated in Ref. 5 for Pu^{3+} (f^5) with intermediate coupling (75% ^6H, 25% ^4G) at $T=0$ using parameter values, $E_1=129.8$ K, $E_2=E_1$, $H_3=-0.0278E_1$, $60B_4=-1.3E_1$. The subsequent experimental data of Lander *et al.* (Ref. 7) at 10 K are shown for comparison. Molecular-field states are shown to the right taking the axis of quantization along the moment direction.

theory. It is this deficiency that we have tried to remove. Since the choice of the phenomenological parameters in our theory[5] provided such good agreement with excitation energies and dispersion shape in subsequent inelastic neutron scattering experiments,[7] we felt that minor "fine tuning" of these parameters or the inclusion of other weak terms in the Hamiltonian would enable us to remove the discrepancies that existed.

In this paper we discuss two different approaches aimed at trying to remove the discrepancies between our theory and the experimental excitation behavior for PuSb. In Sec. II we describe the results of including two-ion quadrupole-quadrupole interactions. Physical and heuristic motivation for the inclusion of such interactions will also be discussed in that section. In Sec. III we motivate and describe in detail efforts to modify the ground state of the free Pu^{3+} ion used in our calculations, in such a way as to represent more accurately the intermediate coupling in the Pu^{3+} ion. Section IV contains comments on the choice of selection rule used to pick scattering processes which determine the two-ion interaction, and also explains the calculation of the g factor in the j-j coupling limit. In Sec. V we present an overview and discussion of our attempts to complete the understanding of the magnetic excitation behavior in PuSb, along with suggestions for future work. Details of the procedure used earlier, as well as suggestions for modifications to that procedure, for the computation of the scattering amplitudes[3] in the cases of L-S and intermediate coupling are discussed in the Appendix, using an example from the case of an ion with two f electrons.

II. QUADRUPOLE INTERACTIONS

As we have already stated, predictive calculations[5] of the energies and dispersion shapes of the magnetic excitations in PuSb are in good agreement with the data from subsequent inelastic neutron scattering experiments.[7] These calculations were performed using the same phenomenological parameters as were used for the equilibrium calculations, and actually predicted absolute excitation energies, i.e., energies were given in terms of the parameter E_1 with a value of 129.8 K as stated in the text and the caption of Fig. 6 of Ref. 5. Figure 1 shows the three lowest modes of the magnetic excitation spectrum predicted[5] [and the molecular-field (MF) levels], as well as the experimentally observed transverse excitations.[7] (We emphasize that there has been no matching of theory and

experiment to obtain Fig. 1. The theoretical curves are exactly as in Ref. 5 without any adjustment.) While the highest of the modes shown in Fig. 1 (solid line labeled L_{41}) was predicted[5] by the theory to have the greatest intensity, the close absolute agreement between the experimental points and the next lower theoretical mode (labeled L_{31}) is indeed remarkable. Note that for **q** perpendicular to the direction of the moment, the experimentally observed excitations have a minimum at the edge of the zone rather than at the center, which is unusual behavior for a ferromagnet. Note too that the theoretical mode labeled L_{31} also has a minimum at the zone edge for **q** perpendicular to the moment.

The major intensity in transverse magnetic excitations (i.e., excitations involving fluctuations perpendicular to the moment) in a Pu^{3+} (f^5) system ($J=\frac{5}{2}$) arises from matrix elements of $J_{\pm}$ between $|\pm\frac{5}{2}\rangle$ and $|\pm\frac{3}{2}\rangle$ single-ion components (identified by the total magnetic quantum number M_J). These components of the ground state and the third excited MF state are what causes the L_{41} mode in our calculated excitation spectrum to have the greatest intensity. A noteworthy feature of the molecular-field eigenstates in this case (and in all cases involving L-S and intermediate coupling, regardless of the choice of phenomenological parameters) is the fact that the $|\pm\frac{1}{2}\rangle$ states do not mix with any of the other states. So the only intensity (of transverse character) in the L_{31} transition arises from the small matrix element of J_- between $\langle -\frac{3}{2}|$ and $|-\frac{1}{2}\rangle$. If state 3 in the MF scheme had some $|\frac{3}{2}\rangle$ or $|-\frac{5}{2}\rangle$ admixture, the intensity of transitions to this state would increase. Simultaneously, the intensity of the L_{41} transition would drop because the coefficients of the $|\frac{3}{2}\rangle$ and $|-\frac{5}{2}\rangle$ components in state 4 would decrease correspondingly. It is then conceivable that most of the intensity might be transferred to the lower of the two transverse modes being considered, i.e., the one that is less dispersive and shows a minimum at the zone edge. Arguing along these lines, we introduced, heuristically, a quadrupole interaction that would mix states with $|M-M'|=2$. This coupling is then represented in the Hamiltonian by the following term:

$$\mathcal{H}_{ij}=Q_{ij}O_2^2(i)\langle O_2^2(j)\rangle \ . \tag{1}$$

Physical motivation for including such a term is provided by the idea that coupling between dynamic lattice distortions and the magnetic excitations probably plays an important role in shaping the magnetic excitations. Single-site coupling between the f electrons and dynamic lattice distortions of ϵ_2 symmetry (i.e., $\sim\epsilon_{xx}-\epsilon_{yy}$, using notation as in Ref. 9) might lead to such two-ion quadrupole interactions. [Equilibrium lattice distortions associated with magnetic ordering are presumably tetragonal ($\sim\epsilon_{zz}$) and couple to single-ion electronic operators of the form $O_0^2(i)$ ($\sim J_z^2$) which only mix states that have the same magnetic quantum numbers.] However, we have included this term in the Hamiltonian without investigating its physical origin in greater detail. We should point out that in general such an interaction will not resolve the problem of the splitting of the intensity with **q** perpendicular to the moment. The intensity shift will occur in both **q** directions, perpendicular and parallel to the moment. Also, since in general the L_{31} and L_{41} modes will not be degenerate at the zone center, the selective splitting of the mode with **q** perpendicular to the moment will not be reproduced by the introduction of this term.

We have considered only the case where such a quadrupole coupling exists between nearest neighbors (only Q_1 nonzero). For small values of Q_1 (Q_1 on the order of $0.001E_1$ or less) the previously found (no quadrupole interactions) ferromagnetic structure is the ground state, but a metastable ferromagnetic state is found in which the lowest MF level has a $|\frac{1}{2}\rangle$ component in addition to the $|\frac{5}{2}\rangle$ and $|-\frac{3}{2}\rangle$ components. As Q_1 is increased, this new metastable state moves down in energy, overtaking the "old" ferromagnetic state. At this point the $|\frac{1}{2}\rangle$ admixture in the MF ground state in this new ferromagnetic structure begins to be large enough to cause a significant shift in the intensity distribution between the L_{31} and L_{41} modes.

However, this approach fails to achieve the desired goal of removing the discrepancies between the predicted and the observed excitation spectra without significantly disturbing the good agreement between theoretical results and experimentally observed equilibrium behavior. While the $|\frac{1}{2}\rangle$ state does get mixed into the ground state, thus reducing the intensity of the nominally L_{41} mode, the intensity shifts more into the much-higher-energy transverse mode labeled L_{51} (involving transitions to one of the crystal-field-split states) than into the lower, nominally L_{31}, transverse mode. Moreover, at about that value of Q_1 where the $|\frac{1}{2}\rangle$ admixture begins to be significant in affecting the excitation spectrum, the long-period antiferromagnetic structure with moment perpendicular to the modulation direction has moved lower in energy than the two ("old" and "new") ferromagnetic structures and is the lowest-lying (in energy) magnetic structure. Hence, contrary to experimental observation, this structure would have to be the one that is observed at zero temperature. Consequently, this approach had to be abandoned.

Some results of this set of calculations are presented in Figs. 2 and 3. Figure 2 shows the predicted magnetic excitation spectrum with $E_1=E_2=|E_1|$; $Q_1=0.0012E_1$; $H_3=-0.0278E_1$; $60B_4=-1.3E_1$. The most intense transverse mode (bold line) is still the third-lowest mode (labeled L_{41}), which is also the most dispersive mode. However, the intensity of this mode has decreased significantly from its intensity in the case with $Q_1=0$. Most of the intensity, however, has shifted into the higher transverse mode labeled L_{51} (involving transitions to a crystal-field-split state) which is about half as intense as the one labeled L_{41} across the zone. The lowest transverse mode L_{31}, is only about half as intense as the highest transverse mode, L_{51}. The admixture of the $|\frac{1}{2}\rangle$ state into the ground state has become significant at this point.

Since dynamic lattice distortions associated with such quadrupole interactions would break the cubic symmetry at a Pu site, and distances to different erstwhile nearest neighbors would be different, presumably the coupling strengths between these nearest neighbors would also be different. We have incorporated this "anisotropy" into

our calculations phenomenologically by making the quadrupole-coupling strength different for nearest neighbors in the $z=0$ plane ($Q_{1\,\mathrm{in}}$) and those out of the plane ($Q_{1\,\mathrm{out}}$). Again, the results were not significantly different from the case without the anisotropy in quadrupole coupling, and the equilibrium properties were thrown far out of agreement with experimental observations before the excitations in the ferromagnetic phase were significantly affected. Figure 3 shows the excitation spectrum for the case when $Q_{1\,\mathrm{out}}=0.5\ Q_{1\,\mathrm{in}}$, while the rest of the parameters are as in Fig. 2.

III. INTERMEDIATE COUPLING AND THE FREE-ION GROUND STATE

While in the cases of L-S and intermediate coupling our previous calculations[5] show a preference for the transverse-polarized antiferromagnetic phase (made up of stacks of ferromagnetically ordered {001} planes with moments along a cube edge but in the plane, i.e., perpendicular to the direction of modulation), in the limit of j-j coupling (where Pu^{3+} would behave qualitatively like Ce^{3+} in our theory[3]) the longitudinally-polarized antiferromagnetic phase (comprising ferromagnetically ordered {001} planes with moments perpendicular to the plane, i.e., parallel to the direction of modulation) is preferred over the transverse-polarized one. Clearly, as the strength of the spin-orbit interaction increases relative to that of the Coulomb interaction, there must be a "crossover point" at which the energies of the two differently polarized antiferromagnetic phases cross. This leads one to believe that in some sense the free-ion ground state of Pu^{3+} in PuSb is closer to the j-j coupling limit than is our description of the intermediate-coupled (IC) ground-state wave function.

At this point we should point out that our description[5] of the intermediate-coupled ground state differs from the exact intermediate-coupled ground state in that for purposes of computing the scattering amplitudes we retained only the dominant ^6H and four ^4G states which make up about 92% of the exact state. We feel that including the remaining terms of the exact intermediate-coupled ground state in the calculations may push the behavior toward favoring the longitudinally-polarized antiferromagnet over the transverse-polarized one. This provides the motivation to try to improve the description of the

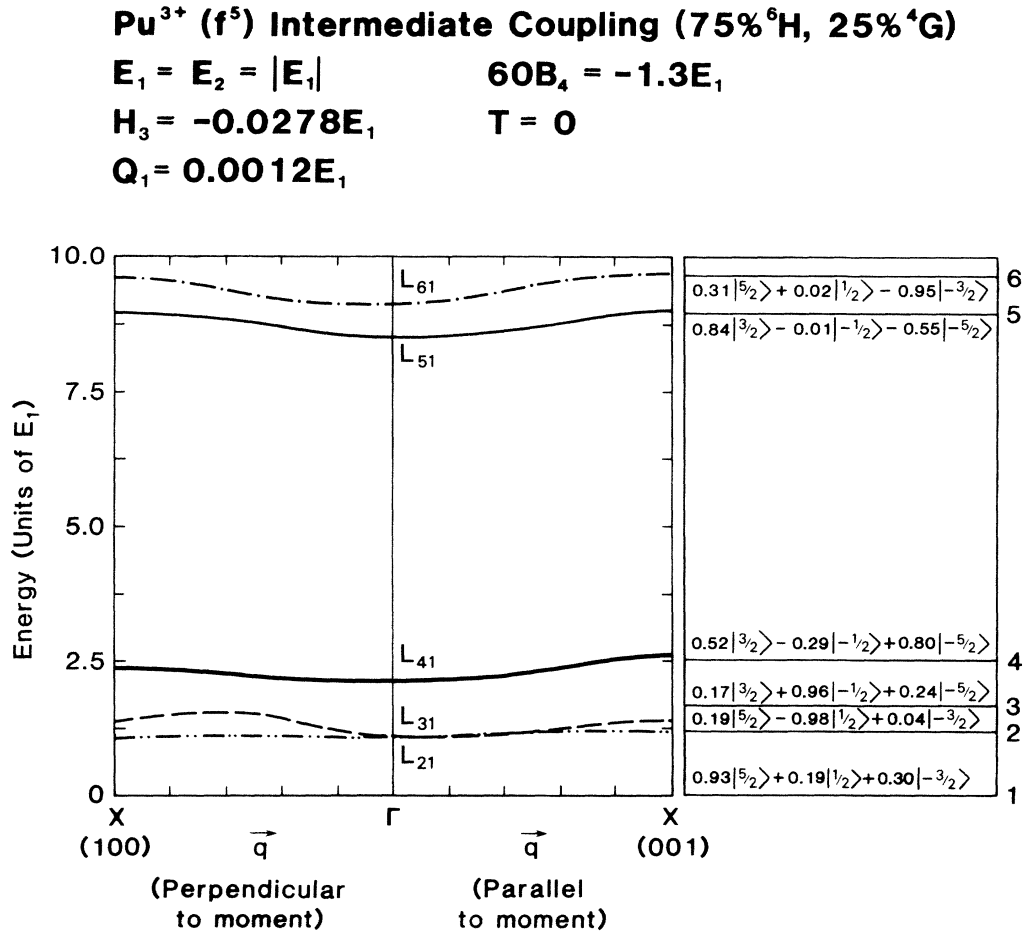

FIG. 2. Magnetic excitations calculated at $T=0$ for a fcc lattice of Pu^{3+} ions with intermediate coupling (75% ^6H, 25% ^4G). Parameters are as in Fig. 6 of Ref. 5 with the addition of quadrupolar coupling ($E_1=E_2=|E_1|$, $H_3=-0.0278E_1$, $60B_4=-1.3E_1$, $Q_1=0.0012E_1$). The most intense excitations are the L_{41} transverse modes (thick solid curve), the next most intense transverse excitations are the L_{51} modes (solid curve). The other modes shown are L_{31} transverse modes (dashed curve), L_{61} longitudinal modes (dotted-dashed curve), and L_{21} quadrupolar modes (dotted-dotted-dashed curve). Molecular-field states are shown to the right.

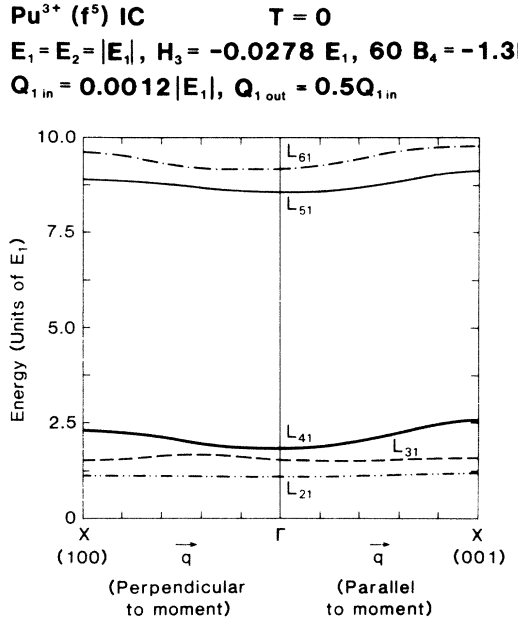

FIG. 3. Magnetic excitations at $T=0$ for a fcc lattice of Pu^{3+} ions as in Fig. 2 with the difference that the quadrupolar interaction is now anisotropic ($E_1=E_2=|E_1|$, $H_3=-0.0278E_1$, $60B_4=-1.3E_1$, $Q_{1\,\mathrm{in}}=0.0012E_1$, $Q_{1\,\mathrm{out}}=0.5Q_{1\,\mathrm{in}}$). Molecular-field states do not differ significantly from those in Fig. 2.

intermediate-coupled state, while at the same time retaining relative ease in computing the scattering amplitudes.

We have already pointed out[5] that as the spin-orbit interaction becomes stronger, the exact ground state (see Table I) is no longer dominated by ^6H and ^4G terms. Including the omitted terms of the exact intermediate-coupled ground state would involve computations essentially similar to those in our earlier approach.[5] The magnitude of the computations, however, would increase greatly because all 28 terms which contribute to a $J=\frac{5}{2}$ state need to be considered; one must then deal with a greatly increased number of Slater determinants in computing the scattering amplitudes. With the basis restricted to the one ^6H and four ^4G terms, it was sufficient to consider only the 15 Slater determinants with $|M_L|=4$ and $|M_S|=\frac{3}{2}$ and those with different values of M_L and M_S that could be obtained by operating on these 15 states with $L_\pm$ and $S_\pm$. When considering all 28 terms one needs to consider the much larger number of Slater determinants which have $|M_L|=1$ (because of the presence of P terms; there are no S terms) and $|M_S|=\frac{1}{2}$ (because of the presence of spin-doublet terms). Once this capability is achieved, however, it will enable us not only to use the exact intermediate-coupled state but also to handle cases of arbitrarily strong spin-orbit coupling, in particular (as a check) the case of spin-orbit interaction only, i.e., the j-j coupling limit, since we know[3] that our theory yields a longitudinally-polarized antiferromagnetic structure in that limit.

One simpler approach that we have already taken in trying to smoothly span the entire range of behavior between the L-S and j-j limits was to effect a more controlled truncation of the wave function. In order to achieve this, we truncated the basis set before the spin-orbit and Coulomb matrices were diagonalized. The basis was restricted to the one ^6H and four ^4G terms that were used in our earlier computations.[5] We calculated the spin-orbit matrix[10] in this restricted basis using tabulated values[11] of the reduced matrix element of the tensor operator $V^{(11)}$. The Coulomb matrix was obtained from Wybourne[12] and again restricted to the truncated basis. For this restricted case of a "pseudo" Pu^{3+} ion, it was then possible to span the entire range from L-S coupling (no spin-orbit coupling) to j-j coupling (no Coulomb interaction) smoothly. The variation of the composition of the ground-state wave function with χ, the ratio of the strength of the spin-orbit interaction to that of the Coulomb interaction, is shown in Fig. 4. It is clear that even in the limit of j-j coupling the ^4G terms do not really dominate, even in this restricted calculation. Consequently, the scattering amplitudes are not very different from those obtained in our approximate IC state or in the L-S limit. The variations of the energies of the ferromagnetic ground state (moments along a cube edge) and the transverse- and longitudinally-polarized long-period antiferromagnetic phases with χ are shown in Fig. 5. While all the levels move to higher energies on approaching the j-j limit, the transverse-polarized antiferromagnetic phase

TABLE I. Composition and g factors of different free-ion ground-state wave functions for Pu^{3+} and for the ground state of Ce^{3+}.

Free-ion ground state	Composition		g factor
Pu^{3+} L-S limit	100% ^6H		0.2857
Pu^{3+} j-j limit	45.3% ^4G,	15.3% ^2F,	0.8011
	14.9% ^4F,	8.5% ^6H,	
	8.5% ^4P,	4.7% ^2D,	
	1.5% ^6F,	0.7% ^6P,	
	0.6% ^4D		
Pu^{3+} exact intermediate coupling	67% ^6H,	25% ^4G, 8% other	0.4152
Pu^{3+} approximate IC[a]	75% ^6H,	25% ^4G	0.3571
Ce^{3+}	100% ^2F		0.8571

[a] As used in Ref. 5.

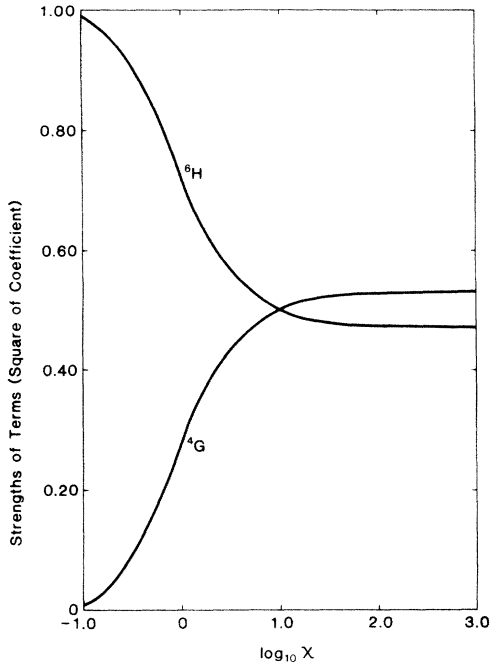

FIG. 4. Variation of composition (in fractions of ^6H and of ^4G respectively, as labeled) of the ground state of $Pu^{3+}(f^5)$ in the truncated basis calculation as a function of χ, the ratio of the strength of the spin-orbit coupling to that of the Coulomb interaction. The spin-orbit term dominates on the right. Note the logarithmic scale on the abscissa.

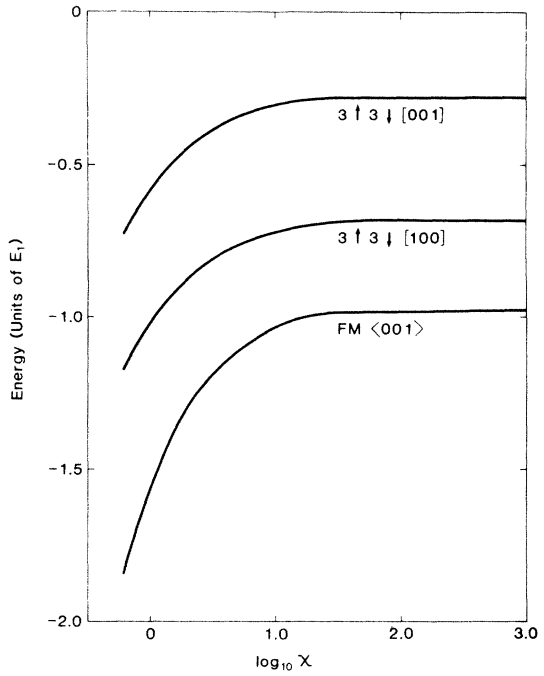

FIG. 5. Variation of the free energies at $T=0$ with $\log_{10}\chi$ for the cube-edge ferromagnet (FM⟨001⟩), the longitudinally-polarized antiferromagnet (3↑,3↓[001]), and the transverse-polarized antiferromagnet (3↑,3↓[100]).

actually moves closer to the ferromagnetic state than does the longitudinally-polarized antiferromagnetic phase. This indicates that this approach to making the free-ion ground state more *j-j*—like probably will not succeed in producing a phase transition to the longitudinally-polarized antiferromagnetic phase with increasing temperature. This is borne out by calculations of the free energies of the various phases as functions of temperature. As discussed in Sec. V below, this failure of the truncated ground-state calculation to produce a longitudinally-polarized antiferromagnetic phase in the spin-orbit-only limit points to the importance of including the complete intermediate-coupled ground state when calculating the scattering amplitudes in order to remove the remaining discrepancies with experiment in PuSb.

IV. COMMENTS ON THE CHOICE OF SELECTION RULE USED TO PICK SCATTERING PROCESSES DETERMINING THE TWO-ION INTERACTION AND ON THE *g* FACTOR IN THE *j-j* COUPLING LIMIT

In the original calculations[1,2] for the Ce^{3+} ion, which has only one *f* electron, it was pointed out that to lowest order in $(1/k_F R)$, which is the typical expansion parameter in Ruderman-Kittel-Kasuya-Yosida (RKKY) type models, the dominant contribution to the two-ion interaction came from processes in which the electron involved in the associated single-site scattering event had magnetic quantum number $m_j=\pm\frac{1}{2}$. Hence, in all subsequent calculations[3] for Ce^{3+}, only contributions from such terms were retained. On extending the theory to systems with more than one *f* electron per ion, it was argued on physical grounds that the reason for this dominance was the large contribution to the two-ion interaction from scattering processes involving *f* electrons with $m_l=0$ as these were the states that pointed their charge densities along the interionic axis (which was taken as the axis of quantization). Consequently, in the *L-S* limit, where free-ion states are expressed as determinantal products (Slater determinants) of single-electron ($l=3$) wave functions labeled by quantum numbers m_l and m_s, only processes involving electrons having $m_l=0$ were considered.[3,5]

However, the $m_j=+\frac{1}{2}$ state, for instance, not only has a contribution from the $m_l=0$, $m_s=\frac{1}{2}$ state, but also has a contribution from the state which has $m_l=1$, $m_s=-\frac{1}{2}$. We wish to point out that as a consequence, the two "selection rules" used in calculating the scattering amplitudes are not necessarily equivalent. This should be realized as one changes from considering the *L-S* limit to considering the *j-j* limit. In the *j-j* limit for Pu^{3+} we applied the $|m_j|=\frac{1}{2}$ selection rule (see the Appendix in Ref. 3). On the other hand, if we were to express the exact *j-j*-coupled ground state in terms of *L-S* coupled states and then calculate the scattering parameters as we presently do for the *L-S* or intermediate-coupled cases (i.e., as was done for the truncated ground state discussed above), we would be applying the $m_l=0$ selection rule as outlined in the Appendix. For the reasons we have just presented, we expect the two computations to yield different results, although if our physical picture for the

dominance of the $m_l=0$ components is correct, we do not expect the difference to be numerically important.

Although we believe that the $m_l=0$ selection rule is the more physically motivated, it is probably simpler to try to apply the $|m_j|=\pm\frac{1}{2}$ selection rule to the $(\{m_l\},\{m_s\})$ states than it is to apply the $m_l=0$ rule to the $(\{m_j\})$ states in order to test the correctness of our expectations. Some preliminary thoughts on how one might apply the $|m_j|=\pm\frac{1}{2}$ selection rule to the L-S (or intermediate-coupled) state are included in the Appendix using the case of an ion with two f electrons ($J=4$) as an example. Details are also presented in the Appendix for the computation of the scattering amplitudes in the L-S and intermediate-coupled cases on applying the $m_l=0$ selection rule to the $(\{m_l\},\{m_s\})$ states.

One other point needs to be noted while considering the differences in behavior at the L-S and j-j limits. It is possible to obtain the j-j coupled ground-state wave function expressed in terms of Russell-Saunders (L-S) terms simply by diagonalizing the spin-orbit matrix alone. As mentioned earlier, in considering the $J=\frac{5}{2}$ manifold, 28 Russell-Saunders terms need to be considered.[11] Upon diagonalizing the resulting 28×28 matrix[10,11] one obtains a decomposition of the ground-state wave function as shown in Table I. Clearly no one small set of terms dominates although the ^4G terms make the greatest contribution. The Landé g factor for this state can be calculated and is also shown in Table I. This is different, though not very significantly, from the g factor ascribed to the j-j coupled Pu^{3+} ground state in our earlier calculations[3] involving the L-S and j-j limits of Pu^{3+}, where it was assumed to be the same as the g factor for Ce^{3+}.

V. DISCUSSION

While our theoretical model for the unusual magnetic behavior of the monopnictides of the light actinides, in particular PuSb, met with remarkable initial success, significant discrepancies as discussed above have remained. Initial optimism regarding a rapid resolution of the remaining problems has proved ephemeral, and until the present time our efforts to remove the discrepancies have not met with success. However, we feel that these efforts have delineated the direction of further progress by providing new insight into the details of our theoretical model, especially with regard to the importance of the detailed intraionic coupling in systems with more than one f electron per ion. While this has been pointed out before[3-5] in the context of PuSb, it is emphasized by the present work. This point is closely connected with the treatment of the f-f correlation in the formalism and, depending on the outcome of calculations using the complete intermediate-coupled ground state, a careful reexamination of this treatment may be called for. Rigorous treatment of the intraionic f-f correlation may become more important as the number of f electrons in the ion is increased. For example, the present formalism gives good results for the anisotropic critical correlation length behavior in uranium systems,[8] but encounters difficulties, as discussed above, for PuSb. Clearly, a more rigorous treatment of the intraionic coupling is called for and should have a high priority in any agenda for future work. The difference in our present treatment of the cases of L-S (and intermediate) and j-j coupling, in that different selection rules ($m_l=0$ versus $m_j=\pm\frac{1}{2}$) are applied in calculating the scattering amplitudes, is also worth serious consideration although the magnitude of the effect of this difference on the predicted equilibrium and excitation behavior may be small.

ACKNOWLEDGMENTS

This research has been supported by the U.S. Department of Energy Grant No. DE-FG05-84ER45134. We appreciate valuable discussion of the experimental excitation behavior of PuSb with G. H. Lander, J. Rossat-Mignod, and W. G. Stirling. We have benefited from discussions with N. Kioussis about his research on the theory of the critical correlation length anisotropy in PuSb and related materials.

APPENDIX: CALCULATION OF SCATTERING AMPLITUDES AND CHOICE OF SELECTION RULES

In this appendix we illustrate the calculation of the scattering amplitudes $A(M,M';m,m')$ in the case of L-S coupling using the case of an ion with two f electrons as an example. It is straightforward to extend the calculation to other ions and to the case of intermediate coupling. In the L-S coupling limit, or whenever the ground state is expressed in terms of Russell-Saunders states, as is usually done for intermediate coupling, in order to calculate the scattering amplitudes, a particular $|J,M_J\rangle$ state needs to be first decomposed into component $|L,S,M_L,M_S\rangle$ states:

$$|J,M_J\rangle=\sum_{M_L}(2J+1)^{1/2}(-1)^{L-S+M_J-2J}\begin{pmatrix}L & S & J\\ M_L & M_J-M_L & M_J\end{pmatrix}|L,S,M_LM_S\rangle\ . \tag{A1}$$

The scattering amplitudes $A(M,M';m,m')$ are then given by

$$A^{MM'}_{mm'}=(2J+1)\sum_{M_L,M_L'}(-1)^{M+M'-2S}\begin{pmatrix}L & S & J\\ M_L & M-M_L & M\end{pmatrix}\begin{pmatrix}L & S & J\\ M_L' & M'-M_L' & M'\end{pmatrix}a(M_L,M_S;M_L',M_S';m,m')\ , \tag{A2}$$

where $a(M_L,M_S;M_L',M_S';m,m')$ is the amplitude of a scattering event in which the ionic state changes from $|M_L,M_S\rangle$ to $|M_L',M_S'\rangle$ (the quantum numbers L and S having been suppressed for brevity) with the exchange of an electron with magnetic quantum number m for one with m'.

In order to compute the amplitudes $a(M_L,M_S;M_L',M_S';m,m')$ the $|M_L,M_S\rangle$ states need to be further decomposed into Slater determinants (SD's) of one-electron wave functions labeled by m_l and m_s. For our example ($L=5$, $S=1$, $J=4$) the following listing gives for each M_J, each of the $|M_L,M_S\rangle$ states contributing to that M_J as a linear combination of SD's labeled by m_l and m_s.

(i) $M_J=4$,

$$|5,-1\rangle=(3^-,2^-)\,,$$

$$|4,0\rangle=[(3^-,1^+)+(3^+,1^-)]/\sqrt{2}\,,$$

$$|3,1\rangle=[(2^+,1^+)+\sqrt{2}(3^+,0^+)]/\sqrt{3}\,;$$

(ii) $M_J=3$,

$$|4,-1\rangle=(3^-,1^-)\,,$$

$$|3,0\rangle=[(2^+,1^-)+(2^-,1^+)]/\sqrt{6}+[(3^+,0^-)+(3^-,0^+)]/\sqrt{3}\,,$$

$$|2,1\rangle=[(3^+,-1^+)+\sqrt{2}(2^+,0^+)/\sqrt{3}\,;$$

(iii) $M_J=2$,

$$|3,-1\rangle=[(2^-,1^-)+\sqrt{2}(3^-,0^-)]/\sqrt{3}\,,$$

$$|2,0\rangle=[(2^+,0^-)+(2^-,0^+)]/\sqrt{3}+[(3^+,-1^-)+(3^-,-1^+)]/\sqrt{6}\,,$$

$$|1,1\rangle=\sqrt{5/21}(1^+,0^+)+3/\sqrt{14}(2^+,-1^+)+\sqrt{5/42}(3^+,-2^+)\,;$$

(iv) $M_J=1$, (A3)

$$|2,-1\rangle=[(3^-,-1^-)+\sqrt{2}(2^-,0^-)]/\sqrt{3}\,,$$

$$|1,0\rangle=\sqrt{5/42}[(1^+,0^-)+(1^-,0^+)]+3/2\sqrt{7}[(2^+,-1^-)+(2^-,-1^+)]+\sqrt{5}/2\sqrt{21}[(3^+,-2^-)+(3^-,-2^+)]\,,$$

$$|0,1\rangle=5/\sqrt{42}(1^+,-1^+)+4/\sqrt{42}(2^+,-2^+)+1/\sqrt{42}(3^+,-3^+)\,;$$

(v) $M_J=0$,

$$|1,-1\rangle=\sqrt{5/21}(1^-,0^-)+3/\sqrt{14}(2^-,-1^-)+\sqrt{5/42}(3^-,-2^-)\,,$$

$$|0,0\rangle=5/2\sqrt{21}[(1^-,-1^+)+(1^+,-1^-)]+2/\sqrt{21}[(2^+,-2^-)+(2^-,-2^+)]+1/2\sqrt{21}[(3^+,-3^-)+(3^-,-3^+)]\,,$$

$$|-1,1\rangle=-\sqrt{5/21}(0^+,-1^+)-3/\sqrt{14}(1^+,-2^+)-\sqrt{5/42}(2^+,-3^+)\,.$$

Wave functions for negative values of M_J can be obtained from the above by changing the signs of all the M_L, M_S, m_l, and m_s.

Now the scattering amplitude $a(3,1;3,0;\frac{1}{2},-\frac{1}{2})$ for the case $f^2(f^1)$ (scattering from f^2 configuration via intermediate virtual f^1 configuration) is obtained by multiplying the coefficient of the SD containing 0^+ ($m_j=\frac{1}{2}$) in the wave function $|3,1\rangle$ with that of the SD containing 0^- ($m_j=-\frac{1}{2}$) in $|3,0\rangle$, giving $\sqrt{2/3}\times\sqrt{1/3}$ ($=\sqrt{2}/3$). In the same way,

$$a(1,0;1,1;-\tfrac{1}{2},\tfrac{1}{2})=5/21\sqrt{2}\,.$$

Note that all the quantum numbers of all the other electrons in the two SD's involved are the same; the scattering being a single-electron process does not affect the other, "spectator," electrons. Note also that since we restrict our attention to events in which the scattered electron (outgoing as well as incoming) has $m_l=0$,

$$a(M_L,M_S;M_L',M_S';m,m')\sim\delta(M_L,M_L')\,.$$

The amplitudes $a(M_L,M_S;M_L',M_S';m,m')$ obtained in this way can be used in Eq. (A2) to calculate the amplitudes $A(M,M';m,m')$.

In order to apply the $|m_j|=\frac{1}{2}$ "selection rule" to a situation such as that described above, we first make the reasonable assumption that the $j=\frac{7}{2}$ single-electron states are much higher above the $j=\frac{5}{2}$ states than the exchange splitting. Then we restrict ourselves to the $j=\frac{5}{2}$ manifold and express a single-electron $|j,m_j\rangle$ state as

$$|\tfrac{5}{2},m_j\rangle=\sqrt{6}\sum_{m_l}(-1)^{15/2+m_j}\begin{pmatrix}3 & \frac{1}{2} & \frac{5}{2}\\ m_l & m_j-m_l & m_j\end{pmatrix}|m_l,m_j-m_l\rangle\,. \tag{A4}$$

Then we make the supposition that the contribution of a scattering event involving an electron with $m_j=\frac{1}{2}$ has a contribution from a component $|m_l,m_s\rangle$ state that is proportional to the amplitude of that state, i.e., the appropriate Clebsch-Gordan coefficient. In that case we have, for example,

$$a(1,0;1,1;-\tfrac{1}{2},\tfrac{1}{2})=\frac{5}{21\sqrt{2}}\times 6\times \begin{bmatrix} 3 & \frac{1}{2} & \frac{5}{2} \\ 0 & -\frac{1}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} 3 & \frac{1}{2} & \frac{5}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{bmatrix} . \tag{A5}$$

Now in addition to the possibility of exchanging an electron with the same m_l $(=0)$ and different m_s values, we also have the possibility of exchanging one with different m_l values (but still with $|m_j|=\frac{1}{2}$). For instance, we could have an electron with quantum numbers (1^-) be replaced by one with (0^-) or with (0^+). As a result, new processes open up and it is no longer true that

$$a(M_L,M_S;M_L',M_S';m,m')\sim\delta(M_L,M_L') .$$

So now, for instance,

$$a(0,1;1,1;-\tfrac{1}{2},\tfrac{1}{2})=(5\sqrt{5}/21\sqrt{2})\times 6\times \begin{bmatrix} 3 & \frac{1}{2} & \frac{5}{2} \\ -1 & \frac{1}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} 3 & \frac{1}{2} & \frac{5}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{bmatrix} . \tag{A6}$$

Consequently, when the amplitudes $A(M,M';m,m')$ are calculated using Eq. (A2), new terms will be included that were not considered when the $m_l=0$ "selection rule" was applied, and the values of the amplitudes will be different.

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