α - γ transition in Ce. II. A detailed analysis of the Kondo volume-collapse model

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The Kondo volume-collapse (KVC) model of the α - γ transition in Ce metal is examined quantitatively using Anderson impurity Hamiltonian parameters obtained from electron spectroscopy. After the hybridization from spectroscopy is scaled by 1.12 to reproduce exactly the experimental zero-temperature susceptibility, the calculation, with no further adjustable parameters, predicts a phase boundary in good agreement with experiment. It is found that the cohesive energy contribution from the hybridization of unoccupied f states and conduction states is quantitatively important in Ce, with a value much larger than the Kondo energy. This contribution is equally large and important for La and Pr, for which the hybridization is often ignored. It is, however, almost spin independent, so that it does not contribute directly to the Kondo energy. Thus the 4f cohesive energy contribution is large in both the α and γ phases, while only the Kondo spin fluctuation energy (and entropy) causes the α - γ transition. This distinguishes the KVC model from the Mott transition model. The Anderson-Hamiltonian-based KVC model is also distinguished from the Kondo-Hamiltonian-based spin-only version of the KVC model in that the latter approach cannot make direct contact with spectroscopic data because charge degrees of freedom are ignored from the outset. This work provides a quantitative confirmation that a unified understanding of the high-energy spectroscopic and low-energy thermodynamic properties of Ce metal has been achieved at the quantitative level.

I. INTRODUCTION

The $\gamma \rightarrow \alpha$ transition in Ce metal, initially discovered at about 8 kbar by room-temperature compression,¹ is extremely interesting because it is the only solid-solid transition in an elemental metal which has a phase boundary terminating at a critical point, in analogy with the wellknown liquid-gas phase boundary. This transition is first order and isostructural, $fcc \rightarrow fcc$, involving the loss of magnetic moments and a volume decrease of about 15% in the α phase.² It is generally agreed that in the γ phase there is one localized 4f electron per cerium atom and that the phase transition involves some change in the state of the 4f electron. Specific mechanisms proposed for the transition include the promotional model,³ the Mott transition model,⁴ and the Kondo volume-collapse (KVC) model.⁵⁻⁷ The first two of these involve energy scales for charge fluctuations and the third involves the energy scale for spin fluctuations. Only the third is even qualitatively consistent with all the known experimental properties of the two phases and of the transition between them.

In the promotional model³ the 4f level moves from below to above the Fermi energy (E_F) in the $\gamma \rightarrow \alpha$ transition, so that the electronic configuration changes from $4f^{1}c^{3}$ to $4f^{0}c^{4}$, where c^{n} denotes *n* conduction electrons per cerium. The relevant energy scales are the binding energy of the 4f electron in the γ phase, and the 4f level width. Theoretical studies⁸ showed that this model requires the 4f binding energy to be ~0.1 eV, so that the f-level width must be much smaller, say, 0.01 eV, in order that the position of the f level, above or below E_F , is well defined. However, photoemission,⁹⁻¹² x-rayabsorption,^{13,14} Compton scattering,¹⁵ and positron an-

nihilation¹⁶ measurements show that there is little difference in the f occupation in the two phases, and that the 4f binding energy is ~ 2 eV, an order of magnitude too large. The width is also much larger, ~ 0.5 eV. The large binding energy was predicted by Johansson⁴ from cohesive energy arguments, and used to motivate his Mott transition picture, in which the 4f electron retains its 4f character, but is described by traditional band theory, in the α phase. In this model the relevant energy scales are those determining the transition from localized behavior to band behavior, i.e., the Coulomb repulsion U between 4f electrons on the same atom, and the 4f level width. Photoemission⁹⁻¹² and bremsstrahlung isochromat spectroscopy¹⁷ show that U is $\sim 6 \text{ eV}$ in both phases and that there is only a small difference in width in the two phases. Experimentally, then, all the charge fluctuation energy scales are too large by an order of magnitude, and too similar in the two phases, to account directly for the transition.

The KVC model involves the spin degrees of freedom, and the relevant energy scale is the spin fluctuation energy of the 4f electrons. This energy scale is much smaller than the energy scale for charge fluctuations, and is in fact the one appropriate to the $\gamma \rightarrow \alpha$ transition. An early suggestion to this effect was made by Edelstein.¹⁸ As proposed by Allen and Martin⁵ in 1982, and further elaborated⁶ in 1985, the KVC model provides a unified view of the magnetic, thermodynamic, and spectroscopic properties of the two phases. The important feature of the model is the use of the Kondo aspects of the Anderson impurity Hamiltonian (AIH),¹⁹ such that the thermodynamic and magnetic properties of each of the two phases are controlled by a single energy scale, the Kondo energy T_K . T_K is an emergent low-energy scale of the

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AIH, and results from *virtual* charge fluctuations of the form $f^1c^3 \rightarrow f^0c^4$ and $f^1c^3 \rightarrow f^2c^2$, i.e., of the kind given a static role in the promotional and Mott transition models. Using an analytical result for T_K that is valid to first order in the inverse degeneracy expansion for the degenerate AIH, for the case of a flat conduction band and an infinite value of U, the model yielded a phase diagram in good agreement with experiment, using Hamiltonian parameters qualitatively consistent with, but not derived explicitly from, spectroscopy. The KVC model has also been studied⁷ using the Kondo Hamiltonian instead of the Anderson Hamiltonian. This approach cannot make contact with the important spectroscopic data because charge degrees of freedom are ignored from the outset.

During the last decade an important theoretical advance in treating the AIH has been made by Gunnarsson and Schönhammer (GS), 20-22 using the 1/N expansion. The GS theory provides a systematic method for calculating the various electron spectra and ground-state properties of the AIH. In addition several electron spectroscopy measurements for α and γ -Ce have appeared in the literature.²³⁻²⁶ The combination of the GS theory and the electron spectroscopy results provides the opportunity to examine the KVC model much more stringently than ever before. In the companion paper²⁷ it has been found that the GS theory provides a remarkably good description of all the spectroscopy data, using the same set of Hamiltonian parameters, if a surface valence change is taken into account. The value of the zerotemperature susceptibility, $\chi(0)$, calculated from bulk Hamiltonian parameters is very close to the experimental value. It was found that the very small T_K values obtained in the analysis of Ref. 26, which posed a serious challenge to the overall consistency of the KVC model, resulted from ignoring the surface contribution in the spectral analysis.

In this paper, we examine the KVC model quantitatively using Anderson impurity Hamiltonian parameters obtained from electron spectroscopy. All the spectroscopy and ground-state calculations are performed to second order in the 1/N expansion with finite U value. After the hybridization from spectroscopy is scaled by 1.12 to get the correct zero-temperature susceptibility, we perform a calculation, with no further adjustable parameters, of the α - γ transition in the KVC model. The calculated phase diagram is in good agreement with the experimental one. We find that the cohesive energy contribution from the hybridization of unoccupied f states and conduction states is quantitatively important in Ce, with a value much larger than the Kondo energy. This contribution is equally large and important in La and Pr, for which the hybridization is often ignored. It is, however, almost the same for the lowest-energy singlet and magnetic states, so that it does not contribute directly to the Kondo energy. Thus the 4f cohesive energy contribution is large in both the α and γ phases, while only the Kondo spin fluctuation energy (and entropy) causes the α - γ transition. This distinguishes the KVC model from the Mott transition model of Johansson,⁴ in which the two phases differ by the presence and absence of the entire 4f cohesive energy. The KVC model using the Anderson Hamiltonian is

also distinguished from the purely spin-based approach,⁷ using the Kondo Hamiltonian, where such important aspects of the charge fluctuations cannot be treated. This work provides a quantitative confirmation that a unified understanding of the high-energy spectroscopic and the low-energy thermodynamic properties of the α and γ Ce has been achieved.

The remainder of this paper is organized as follows. Section II summarizes the results of the Anderson impurity Hamiltonian analysis of the α - and γ -Ce spectra, obtained in the companion paper.²⁷ Section III gives the details of the KVC calculation using the spectroscopic parameters, and Sec. IV discusses the results of the calculation. Section V states the conclusions. In Appendix A we present the Anderson impurity Hamiltonian analysis of the La and Pr spectra, which is needed in the KVC calculation, as discussed in detail later. Appendix B gives a pedogogical discussion²⁸ of the asymmetry between the f^0 and f^2 states in Ce.

II. SPECTROSCOPY RESULTS

In the Anderson impurity Hamiltonian, the f electrons in a localized state of energy ε_f and degeneracy N hybridize with the conduction electrons via a matrix element $V(\varepsilon)$, and repel each other with Coulomb energy U. The energy dependence of $V(\varepsilon)$ for each of the two phases has been calculated in the local spin-density approximation.²⁹ The bulk Hamiltonian parameters and ground-state properties obtained from the analysis of the companion paper²⁷ are summarized in Table I. The parameter Δ is the average of $\pi |V(\varepsilon)|^2$ over a 3-eV range below E_F , and n_f is the *f*-level occupation. For comparison, the experimental $\chi(0)$ values for both phases are also shown in the table. Because $\chi(0)$ is not directly accessible for γ -Ce, the experimental value given here has been deduced from the quasielastic-neutron-scattering linewidth Γ ,³¹ using the theoretical result³² that for the temperature of interest $\Gamma \approx T_K$ and the following relation:^{33,27}

$$\chi(0) = C \frac{1 - w(f^0)}{T_K} , \qquad (1)$$

where C is the Curie constant for the spin-orbit split state $j = \frac{5}{2}$, and $w(f^0)$ is the occupation of the f^0 configuration. The $\chi(0)$ values calculated from the spectroscopic parameters are slightly larger than the experimental ones. One possible reason, as stated elsewhere³⁴ in detail, is the renormalization of $V(\varepsilon)$ due to the

TABLE I. Anderson impurity Hamiltonian parameters and ground-state properties of α and γ Ce.

	α-Ce	γ-Ce
ε_f (eV)	$-1.27{\pm}0.04$	$-1.27{\pm}0.04$
\dot{U} (eV)	6	6
Δ_{ave} (meV)	66.3±2.0	32.2±0.4
n _f	0.861±0.015	$0.971 {\pm} 0.006$
$\chi(0)$ (10 ⁻³ emu/mol)	$0.70 {\pm} 0.10$	8.0±1.4
$\chi(0)_{expt}$ (10 ⁻³ emu/mol)	0.53 (Ref. 30)) ~ 4.3 (see text)

Coulomb interaction between f and conduction electrons. To get the correct $\chi(0)$ value, therefore, requires a small increase for the hybridization determined from spectroscopy. This renormalization of the hybridization Δ is 1.12 for both phases, and changes the n_f values to 0.843 and 0.957 for the α and γ phases, respectively. Thus both phases are still in the Kondo regime where n_f is ≥ 0.8 , and so the change in n_f is far less than expected in the promotional model. Hereafter, there are no other parameters adjusted throughout this calculation.

III. KVC CALCULATION

In the KVC model, the free energy of the system is written $as^{5,6}$

$$F(v,T) = E_0(v) + E_{g,s}(v) + E_K(v,T) , \qquad (2)$$

where v and T are the volume and temperature. $E_0(v)$ is the cohesive energy contribution from all sources except the f electrons. The second term is the ground-state energy of the AIH used to describe the f electron, and includes both spin and charge fluctuation contributions. The third term is the temperature-dependent part of the free energy from the f electrons, which is related to the f-electron specific heat. The specific heat of the lattice and conduction electrons is very small compared with that of the f electrons, and so the temperature dependence of the E_0 term is ignored. In previous KVC calculations,^{5,6} $E_0(v)$ and $E_{g.s.}(v)$ were regarded as "normal" and "anomalous" contributions to the cohesive energy. $E_0(v)$ was found empirically by averaging the bulk moduli of La and Pr, which are, respectively, the left and right neighbors of Ce in the periodic table, and which do not display anomalous behavior. $E_{g.s.}(v)$ was found as the ground-state energy of the Anderson model with infinite U.

In the present calculation with finite U, it is essential to modify the previous treatment of $E_0(v)$ to account for the large contribution of the $4f^2$ states to the ground-state energy of the AIH, i.e., to $E_{g.s.}(v)$. This 4f contribution to the total cohesive energy is of similar size for La, Ce, and Pr because the hybridization and f-state affinity energy have similar values in the three materials. It is therefore an important part of the elastic energy of La and Pr. To avoid double counting this large energy in the first two terms of Eq. (2) we calculate $E_0(v)$ as

$$E_0(v) = \frac{B_N}{2} (v - v_N)^2 - E_{g.s.}^{\text{La,Pr}}(v) . \qquad (3)$$

The elastic energy term is the "normal" term of previous KVC calculations, with $B_N = 280$ kbar and $v_N = 36$ Å³ being the averages of the La and Pr bulk moduli and volumes,³⁵ respectively. $E_{g.s.}^{La,Pr}(v)$ is the average of the 4f contributions to the elastic energies of La and Pr. A GS analysis adapted to the La and Pr electron spectra is described in Appendix A, and the Hamiltonian parameters obtained are used to calculate $E_{g.s.}^{La,Pr}(v)$ from the ground-state energy of the AIH for La and Pr. As discussed in detail in the next section, only the Kondo part of the total 4f energy is important for the α - γ transition.

The temperature-dependent part of the free energy in Eq. (2) is, from a standard thermodynamic relation,

$$E_{K}(v,T) = \int_{0}^{T} dT' C_{v}(v,T') - T \int_{0}^{T} dT' \frac{C_{v}(v,T')}{T'} .$$
 (4)

As in the previous KVC calculations,^{5,6} the specific heat is taken from the Bethe ansatz result of Rajan³⁶ for the Kondo Hamiltonian with N = 6. In this case, the result is a universal function $C_v(T/T_K)$.³⁷ In the extreme Kondo limit $(n_f = 1)$, the Anderson impurity Hamiltonian is equivalent to the Kondo Hamiltonian.³⁸ Although Bethe ansatz calculations for the thermodynamic properties of the Anderson Hamiltonian with infinite U value are also available,³⁹ the lack of universality and the limit to infinite U value prevent using the result in this work. For the parameter ranges of α and γ Ce, the contribution to the total specific heat from charge fluctuation is estimated to be ~10%.³⁹ Thus the use of the Kondo result, which has no charge fluctuation degree of freedom, is appropriate.

In calculating the α - γ transition, all Hamiltonian parameters are fixed except that the hybridization changes with the volume, in accordance with the result from spectroscopy that only the hybridization value is different in the two phases. As done previously,⁶ the inverse power-law dependence of hybridization on volume is approximated by a linear interpolation of the values in the α and γ phases, i.e.,

$$\Delta_{v}(\varepsilon) = \frac{v_{\gamma} - v}{v_{\gamma} - v_{\alpha}} \Delta_{\alpha}(\varepsilon) + \frac{v - v_{\alpha}}{v_{\gamma} - v_{\alpha}} \Delta_{\gamma}(\varepsilon) .$$
 (5)

The ground-state energy $E_{g.s.}$ and the zero-temperature susceptibility $\chi(0)$ are then calculated as a function of volume v. T_K is derived from $\chi(0)$ using Eq. (1). $E_{g.s.}^{\text{La,Pr}}(v)$ is calculated for the Hamiltonian parameters obtained in Appendix A. The volume and energy dependences of the hybridization for La and Pr are taken to be the same as for Ce [Eq. (5)]. However, the magnitude of the hybridization has to be scaled from the Ce value by 1.79 and 0.64 for La and Pr, respectively, as determined by fitting the La and Pr spectra at their normal volumes. The decrease in hybridization from La to Ce to Pr is probably due to the decreasing orbital size of the 4fstates with increasing atomic number in the rare-earth series.⁴⁰ All the free-energy contributions are inserted into Eq. (2), and the pressure-vs-volume isotherms are calculated from the thermodynamic relation,

$$P(v,T) = -\frac{\partial F(v,T)}{\partial v} .$$
(6)

IV. RESULTS AND DISCUSSIONS

The role of the various f contributions to the cohesive energy can be understood with the aid of Fig. 1. The two lower curves show the volume dependence of $E_{g.s.}$ and $E_{g.s.}^{La,Pr}$. In the volume region of the figure, $E_{g.s.}^{La,Pr}$ is a straight line, and its magnitude is comparable to $E_{g.s.}$ for Ce. $E_{g.s.}$ for La is entirely due to the mixing of $4f^1$ states into the ground state, $E_{g.s.}$ for Pr is almost entirely due



FIG. 1. The curves in the figure from bottom to top are identified as (a)-(d): (a) Singlet ground-state energy of Ce, $E_{g.s.}$, (b) *f*-configuration contribution to the cohesive energy in La and Pr, $E_{g.s.}^{\text{La,Pr}}$, (c) difference of (a)-(b), and (d) minus the Kondo temperature of Ce, $-T_K(v)$, as a function of reduced volume v/v_N .

to mixing of f^3 states into the ground state, with negligible contribution from the f^1 states. $E_{g.s.}^{La,Pr}$ can be thought of as an estimate of the f^2 contribution for Ce, which is large even though the f^2 ground-state occupation is small, ~3% for α -Ce at $T \sim 20$ K and pressure ~0 kbar. $E_{g.s.} - E_{g.s.}^{La,Pr}$ can be thought of as an estimate of the f^0 contribution to the ground-state energy in Ce.

It is very important that, unlike the f^0 contribution, the f^2 contribution is almost independent of whether or not the ground state is a singlet. The energy lowering of the singlet below the magnetic state, i.e., the Kondo energy, is mainly from hybridization of f^0 into the ground state in the case of Ce. It is the Kondo energy that is essential for the α - γ transition, and it is this energy that is much larger for Ce than for La or Pr. The asymmetry between the f^0 and f^2 states is exclusively for the large-Nlimit, and has been discussed in detail by Gunnarsson and Schönhammer.^{22,33,21} In Appendix B we present a pedogogical discussion of this.

Using Eq. (3), the first two terms of Eq. (2) can be written as

$$E_{0}(v) + E_{g.s.}(v) = \frac{B_{N}}{2} (v - v_{N})^{2} + [E_{g.s.}(v) - E_{g.s.}^{La, Pr}(v)] .$$
(7)

The quantity in brackets is essentially the Kondo energy of Ce, as can be seen from the top two curves of Fig. 1, which show that $k_B T_K(v)$ and $[E_{g.s.}(v) - E_{g.s.}^{La,Pr}(v)]$ are very nearly the same. For a first-order GS treatment of the AIH with infinite U, as done in the previous KVC calculations,^{5,6} $E_{g.s.}^{La,Pr}(v)$ is zero, and $E_{g.s.}(v)$ equals $k_B T_K$. Thus $[E_{g.s.}(v) - E_{g.s.}^{La,Pr}(v)]$ is the appropriate generalization for the "anomalous" 4f energy term of the previous KVC calculations. Note that quantities with a significant Kondo contribution are not linear in v, reflecting a rapid dependence of the Kondo energy on the AIH parameters. In the simplest case of a first-order GS treatment with infinite U and constant hybridization V, and near the extreme Kondo limit with $n_f \sim 1$, this dependence is exponential in $(-\varepsilon_f / N_f \rho V^2)$.

Shown in Fig. 2 are the isotherms calculated using Eq. (6). The calculation predicts a first-order phase transition with volume changes from $v_{\gamma}/v_N = 0.96$ to $v_{\alpha}/v_N = 0.87$ at room temperature. The experimental values of the room-temperature volume for the two phases are marked as arrows. The phase boundary, constructed from Fig. 2 using the equal-area scheme,⁴¹ is compared with the experimental one in Fig. 3. The reported experimental error bars² for the critical point at $T \sim 600$ K and $P \sim 20$ kbar are shown by the box size, and this provides an estimate of the uncertainty in the experimental phase boundary. It is important to note that the slopes of the calculated and experimental phase boundaries are approximately equal. According to the Clapeyron equation, if the volume change is correctly predicted this means that the change of the spin fluctuation entropy during the phase transition is the right amount of entropy needed for this transition. This can also be confirmed in a different way. From the Clapeyron equation the entropy change during the phase transition is $\Delta S = \Delta V dP / dT$. Knowing the experimental volume change and the slope of the experimental phase boundary, ΔS is estimated to be $\approx 1.54k_B$, where k_B is the Boltzmann constant. The entropy for the $J = \frac{5}{2}$ state, appropriate for Ce, is $S = k_B \ln 6 \approx 1.79 k_B$, which is very close to the value required for the transition. These arguments are strong evidence that the Kondo effect is indeed the dominant force for the transition, and that the charge fluctuation entropy is negligible. The calculated phase boundary ter-



FIG. 2. *P-V* isotherms for *T* from 0 to 640 K with equal increments $\Delta T = 40$ K. The arrows mark the experimental equilibrium volumes of the α and γ phases at room temperature. The horizontal dashed lines indicate the equilibrium pressure for a given temperature on the phase diagram.



FIG. 3. Comparison between experimental (Ref. 2) and the calculated phase diagrams. The box around the experimental critical point indicates the uncertainty.

minates in a critical point near 520 K and 13 kbar, close to the experimental one. In the theory, the critical point pressure is very sensitive to the correction $E_{g.s.}^{\text{La,Pr}}$. Small adjustments of the spectroscopically determined La and Pr parameters could be made to produce agreement with the experimental critical point, but such fine tuning has not been done here. The second critical point at a negative pressure, a prediction specific to the KVC model, is observed in alloys,⁴² where it is shifted to the physical observable positive pressure region. The previous KVC calculations^{5,6} gave a good phase boundary description because the important f^2 contribution to the ground-state energy $E_{g.s.}(v)$ in Ce, neglected for infinite U, roughly cancels the correction to $E_0(v)$ from the La and Pr f states [Eqs. (2) and (3)], and because adjustable parameters were used in the calculation.

Finally, we turn our attention to the implications of density-functional theory (DFT) for discerning the appropriate model of the $\gamma \rightarrow \alpha$ transition, a subject which is often misunderstood and deserves some comment. Published efforts⁴³⁻⁴⁶ using the local density approximation (LDA) to the DFT have not been very successful. There was not clear evidence for a first-order transition and the predicted transition pressure is over an order of magnitude larger than the experimental value. The most recent calculation,⁴⁷ which includes the effects of spin polarization within the LDA and includes spin-orbit coupling, was able to produce a first-order transition at zero temperature, although the predicted pressure is at ~ -30 kbar as compared to the experimental value of ~ -7 kbar estimated from the phase diagram. We speculate that the difficulties of approximate DFT theories to date in reproducing the transition pressure is that they do not take out the appropriate small spin fluctuation part of the total 4f cohesive energy. They still retain too much of the spirit of the Mott transition model, in which the total 4f cohesive energy produces the phase transition. Indeed, in the present KVC calculation, failure to incorporate the $E_{g.s.}^{La,Pr}$ term in the free energy shifts the α - γ transition line by 40 kbar to negative pressures. Nonetheless, an exact DFT calculation should reproduce the zero-temperature transition correctly. We point out that an exact DFT calculation is not synonymous with the Mott transition model. Such an exact calculation would incorporate for both phases the spin fluctuation effects which are missed in the current approximate DFT treatments, and which are not part of the Mott transition model as it has been described. But it seems possible that some approximate version of the DFT might treat the interplay of spin and charge fluctuations well enough to give a good description of the phase, such as the magnetic susceptibilities.

V. CONCLUSION

In summary, we have used the Anderson impurity Hamiltonian parameters from electron spectroscopy to calculate the α - γ transition in Ce in the KVC model. After the hybridization obtained from spectroscopy is scaled by 1.12 to reproduce exactly the experimental zero-temperature susceptibility, the calculation, with no further adjustable parameters, predicts a phase boundary in good agreement with the experimental one. It is found that the cohesive energy contribution from the hybridization of unoccupied f states and conduction states is quantitatively important in Ce, as well as in La and Pr, for which the hybridization is often ignored. This contribution to the 4f cohesive energy is, however, almost spin independent, so that it does not contribute directly to the Kondo energy. It is the Kondo spin fluctuation energy and entropy in Ce that are responsible for the α - γ transition, and this distinguishes the KVC model from the Mott transition model where the spin and charge contributions are not separated, and where the entire 4fcohesive energy turns on and off at the phase transition. The KVC model using the Anderson Hamiltonian is also distinguished from the pure spin version⁷ of the KVC model using the Kondo Hamiltonian, in that the latter approach cannot make direct contact with spectroscopic data and the influence of the f^2 state to the cohesive energy mentioned above cannot be discussed. This work provides a quantitative confirmation that the Anderson-Hamiltonian-based KVC model can explain the α - γ transition in Ce, and that a unified understanding of the high-energy spectroscopic and the low-energy thermodynamic properties of the α and γ Ce has been achieved at the quantitative level.

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APPENDIX A: AIH ANALYSIS OF La AND Pr SPECTRA

In this appendix we present the results of a GS analysis of the electron spectra for La and Pr. Although a generic calculation for Pr 4f photoemission spectroscopy (PES) was done previously,⁴⁸ there are no calculations for 4fbremsstrahlung isochromatic spectroscopy (BIS) and 3d x-ray photoemission spectroscopy (XPS). It has been found that surface emission is not negligible in quantitative spectral analysis,^{49,27} especially for α -like compounds. This surface emission contribution is most important for the valence band spectrum which is often taken at low photon energies. BIS and 3d XPS spectra taken at Al $K\alpha$ energy (1486.6 eV) are less surface sensitive because the electrons involved have large kinetic energies and therefore have large escape depth. For La and Pr, which are very γ -like with weak hybridization, we therefore use the BIS and 3d XPS spectra for our fitting and ignore the surface emission. Detailed methods of analyzing the spectra are presented in Refs. 21, 22, and 27.

The hybridization parameters $\Delta(\epsilon)$ for La and Pr were

FIG. 4. Gunnarsson-Schönhammer calculation (solid line) and experimental data (dots) of La and Pr BIS and 3d XPS spectra. The inelastic background and conduction density of states in the BIS data is taken as straight lines. The experimental data are taken from the following works: BIS, Ref. 51; La 3d XPS, Ref. 52; and Pr 3d XPS, Ref. 53.

TABLE II. And erson impurity Hamiltonian parameters and ground-state properties of La and Pr. For Pr ε_f is the energy difference $E(f^2) - E(f^1)$.

	La	Pr
ϵ_{f} (eV)	5.2	-3.3
\dot{U} (eV)		7.3
U_{fc} (eV)	8.5	11.3
Δ_{ave} (meV)	28.7	21.8
n_{f^0}	0.988	
n_{f^1}	0.012	0.003
n_{f^2}		0.984
n ₆₃		0.013
$\vec{E}_{g.s.}$ (eV)	0.067	0.073

taken to be the same as those of α and γ Ce, extrapolated to the volumes of La and Pr $[v = 37.5 \text{ \AA for La}, \text{ and } 34.6]$ Å for Pr (Ref. 50)] using Eq. (4). This approach relies on the fact that the details of the energy dependence of $\Delta(\varepsilon)$ are not very important for BIS and 3d XPS spectra. The extrapolated theoretical hybridization ($\Delta_{ave} = 16 \text{ meV}$ for La, and 34 meV for Pr) has to be scaled in order to fit the spectrum. Figure 4 shows the comparison between the calculated (solid line) and experimental⁵¹⁻⁵³ (dotted) 4fBIS and 3d XPS spectra. The fitting parameters and the occupations for the various f configurations are shown in Table II. The position of the $f^0 \rightarrow f^1$ peak in the La BIS spectrum determines the La ε_f value. The La 3d XPS spectrum has a spin-orbit splitting energy of 16.2 eV. The size of the f^1 peak on the low-binding-energy side is a measure of the hybridization strength. For Pr, the position of the $f^2 \rightarrow f^1$ ionization peak in the valence band spectrum⁵⁴ (taken with photon energy 80 eV, not shown here) determines the Pr $\varepsilon_f = E(f^2) - E(f^1)$ value. The multiplet splittings in the Pr BIS spectrum⁵¹ are included, and the average position of the $f^2 \rightarrow f^3$ peak determines the U value. The Pr 3d XPS spectrum has a spin-orbit splitting of 20.4 eV. The $3d_{3/2}$ peak has final-state multiplet and energy loss structures at -25 eV and -15 eV, respectively. These structures are not included in the theory, and the fitting is therefore done for the $3d_{5/2}$ peak.

APPENDIX B: ASYMMETRY BETWEEN f^0 AND f^2 STATES

In this appendix we present a pedagogical discussion²⁸ of the asymmetry between the f^0 and f^2 states in Ce. This asymmetry is exclusively for the large-N limit, and has been discussed in detail by Gunnarsson and Schönhammer^{22,33,21} in both analytical and numerical forms.

In the $N \rightarrow \infty$ limit, f^0 , f^1 , and f^2 states with no electron-hole excitations in the conduction band, denoted by GS as "first-order," form a complete set of basis states for the ground state. We denote these three states by $|0\rangle$, $|\varepsilon\rangle$, and $|\varepsilon\varepsilon'\rangle$, respectively, where ε and ε' are the energy of the valence holes in the f^1 and f^2 states, for which one and two conduction electrons are transferred to the f lev-



el, respectively. Both ε and ε' are variables having the range from the Fermi energy to the bottom of the valence band. Thus the $|\varepsilon\rangle$ and the $|\varepsilon\varepsilon'\rangle$ states are single and double continua, while the $|0\rangle$ state is a single state.

Consider first the $f^0 - f^1$ coupling. The lowest-energy $|\varepsilon\rangle$ state is $|E_F\rangle$. The f^0 to f^1 hopping matrix element is $\propto 1/\sqrt{v}$, from the normalization of the Bloch wave function, where v is the volume of the whole solid. The perturbation of the $|E_F\rangle$ state by coupling to the $|0\rangle$ state then vanishes as v goes to infinity. In the 1/N expansion theory, this is avoided by making a linear combination of the $|\varepsilon\rangle$ states, i.e., summing over a part of the continuum from E_F to some energy $E_F - T_0$. The coefficient of the basis states in this linear combination is $\propto 1/\sqrt{v}$, from the normalization of the summed state. Because $|\varepsilon\rangle$ is a continuum, the sum is an integral over energy, and is $\propto v$, from a phase space argument, which then cancels the 1/v coming from the matrix element and the basis state coefficient. The f^0 - f^1 hopping is therefore stabilized by making this sum, and the hopping matrix element is $\propto \sqrt{T_0}$. However, making the sum also drives the energy of the summed state up because states with higher energies are mixed in. The competition between these two effects determines the cutoff energy T_0 . In addition each $|\varepsilon\rangle$ state in the sum has by construction a zero z component of the angular momentum, but is not a singlet. By summing over all channels of the N degeneracy, one makes a singlet state, which is energetically favorable because it increases the coupling to the $|0\rangle$ state from V to $\sqrt{N}V$. The f^0 coupling to the singlet f^1 ground state is therefore \sqrt{N} times stronger than that to the magnetic f^1 state, and this difference gives rise to the Kondo effect. For the f^0 to singlet f^1 coupling it is found²¹ that the cutoff energy T_0 discussed above is approximately the Kondo temperature T_K .

When considering the f^1 - f^2 coupling, there are, however, the following differences.

(1) It is not necessary to make a sum over $|\varepsilon\rangle$ states to get a finite $f^1 - f^2$ coupling, because $|\varepsilon\varepsilon'\rangle$ is a double continuum so that the state $|E_F\rangle$ couples to a continuum of $|E_F\varepsilon'\rangle$ states. Summing over this continuum ε' then generates the volume factor needed to stabilize the perturba-

tion of the $|E_F\rangle$ state as the volume goes to infinity. The f^1-f^2 coupling is therefore a much bigger effect than the f^1-f^2 coupling, really because each $|\varepsilon\rangle$ state couples to an entire continuum of $|\varepsilon\varepsilon'\rangle$ states rather than just one $|0\rangle$ state.

(2) The f^1 to f^2 coupling does not depend on whether the f^1 state is magnetic or not, i.e., it does not enhance the coupling to make a singlet by summing the $|\varepsilon\rangle$ over the N degenerate channels. In this case, it is easy to show that the summation just divides up the weight of the ground state into N pieces, with each of them coupling the same way to the $|\varepsilon\rangle'$ states. Therefore, if the $|0\rangle$ state is turned off, the $f^1 - f^2$ coupling would give exactly the same contribution to the ground-state energy for magnetic f^1 as for singlet f^1 , and there is no Kondo effect. Figure 15 of Ref. 21 shows this large $f^1 - f^2$ contribution to the cohesion even when the weight of the f^0 state is zero, i.e., the f^0 state is turned off.

state is zero, i.e., the f^0 state is turned off. (3) When both the f^0 and f^2 states are allowed to mix with the f^1 state, there is an interplay between the f^0-f^1 and f^1-f^2 coupling such that the f^1-f^2 coupling does finally have an effect on the Kondo energy, as shown in Refs. 33 and 22. But this effect is indirect, and only under very strict conditions³³ are the f^2 and f^0 contributions to the Kondo energy symmetric, as in the result obtained from the Coqblin-Schrieffer⁵⁵ transformation for N > 2. These conditions are $|\varepsilon_f|, |U + \varepsilon_f| >> B, \Delta$, where *B* is the width of the valence band. For Ce, $B \sim 3$ eV, and these conditions are not met (see Table I).

As we pointed out from the beginning, the asymmetry between the f^0 and f^2 states discussed in this appendix is exclusively for the large-N limit. For small N, higherorder states, i.e., states with electron-hole excitations in the conduction band, must be included in expanding the ground state, and in consequence the asymmetry between the f^0 and f^2 states begins to disappear. For the special case of N=2, there is electron-hole symmetry between the f^0 and f^2 states, and they contribute to the groundstate energy and the Kondo energy symmetrically. In this case, the symmetric result of the Schrieffier-Wolff transformation for N=2 does not require the strict conditions given for the large-N limit.

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- ²Handbook on the Physics and Chemistry of Rare Earths, edited by K. A. Gschnerdner and L. R. Eyring (North-Holland, Amsterdam, 1978), Vol. I; see D. C. Koskenmaki and K. A. Gschneidner, *ibid.*, Chap. 4, p. 337.
- ³W. H. Zachariasen (unpublished) quoted in A. W. Lawson and T. Y. Tang, Phys. Rev. 76, 301 (1949); L. Pauling, J. Am. Chem. Soc. 69, 542 (1947).
- ⁴B. Johansson, Philos. Mag. 30, 469 (1974).
- ⁵J. W. Allen and R. M. Martin, Phys. Rev. Lett. 49, 1106 (1982).
- ⁶R. M. Martin and J. W. Allen, J. Magn. Magn. Mater. **47&48**, 257 (1985).
- ⁷M. Lavagna, C. Lacroix, and M. Cyrot, Phys. Lett. **90A**, 210 (1982); J. Phys. F **13**, 1007 (1983).

- ⁸R. Ramirez and L. M. Falicov, Phys. Rev. B 3, 2425 (1971); B. Coqblin and A. Blandin, Adv. Phys. 17, 281 (1968).
- ⁹J. W. Allen, S.-J. Oh, I. Lindau, J. M. Lawrence, L. I. Johansson, and S. B. Hagström, Phys. Rev. Lett. 46, 1100 (1981); J. W. Allen, S.-J. Oh, I. Lindau, M. B. Maple, J. F. Suassuna, and S. B. Hagström, Phys. Rev. B 26, 445 (1982).
- ¹⁰M. Croft, J. H. Weaver, D. J. Peterman, and A. Franciosi, Phys. Rev. Lett. **46**, 1104 (1981).
- ¹¹N. Matersson, B. Rheil, and R. D. Parks, Solid State Commun. **41**, 573 (1982).
- ¹²D. Wieliczka, J. H. Weaver, D. W. Lynch, and C. G. Olson, Phys. Rev. B 26, 7056 (1982).
- ¹³K. R. Bauschspiess, W. Kboksch, E. Holland-Moritz, H. Launois, R. Pott, and D. K. Wohlleben, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 417.

¹P. W. Bridgman, Proc. Am. Acad. Arts Sci. 62, 207 (1927).

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- ¹⁴J. C. Fuggle, F. U. Hillebrecht, J.-M. Esteva, R. C. Karnatak, O. Gunnarsson, and K. Schönhammer, Phys. Rev. B 27, 4637 (1983).
- ¹⁵U. Kornstädt, R. Lässer, and B. Lengeler, Phys. Rev. B 21, 1898 (1980).
- ¹⁶D. Gustafson, J. McNutt, and L. Roellig, Phys. Rev. 183, 435 (1969).
- ¹⁷J. K. Lang, Y. Baer, and P. A. Cox, Phys. Rev. Lett. **42**, 74 (1978); P. A. Cox, J. K. Lang, and Y. Baer, J. Phys. F **11**, 113 (1981); J. K. Lang, Y. Baer, and P. A. Cox, *ibid*. **11**, 121 (1981); Y. Baer, H. R. Ott, J. C. Fuggle, and L. E. DeLong, Phys. Rev. B **24**, 5384 (1981).
- ¹⁸A. S. Edelstein, Phys. Rev. Lett. **20**, 1348 (1968).
- ¹⁹P. W. Anderson, Phys. Rev. **124**, 41 (1961).
- ²⁰O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. 50, 604 (1983).
- ²¹O. Gunnarsson and K. Schönhammer, Phys. Rev. B 28, 4315 (1983).
- ²²O. Gunnarsson and K. Schönhammer, Phys. Rev. B 31, 4815 (1985).
- ²³E. Wuilloud, H. R. Moser, W.-D. Schneider, and Y. Baer, Phys. Rev. B 28, 7354 (1983).
- ²⁴D. M. Wieliczka, C. G. Olson, and D. W. Lynch, Phys. Rev. B 29, 3028 (1984).
- ²⁵F. U. Hillebrecht, J. C. Fuggle, G. A. Sawatzky, and M. Campagna, Phys. Rev. B 30, 1777 (1984).
- ²⁶F. Patthey, B. Delley, W.-D. Schneider, and Y. Baer, Phys. Rev. Lett. 55, 1518 (1985).
- ²⁷L. Z. Liu, J. W. Allen, O. Gunnarsson, N. E. Christensen, and O. K. Andersen, Phys. Rev. B 45, 8934 (1992).
- ²⁸O. Gunnarsson (unpublished).
- ²⁹O. Gunnarsson, N. E. Christensen, and O. K. Andersen, J. Magn. Magn. Mater. **76&77**, 30 (1988).
- ³⁰J. W. Lawrence and R. D. Parks, J. Phys. C 4, 249 (1976).
- ³¹S. M. Shapiro, J. D. Axe, R. J. Birgeneau, J. M. Lawrence, and R. D. Parks, Phys. Rev. B 16, 2225 (1977); B. D. Rainford, B. Buras, and B. Lebech, Physica B&C 86-88B, 41 (1977); C. Stassi, T. Gould, O. D. McMaster, K. A. Gschneider, and R. M. Nicklow, Phys. Rev. B 19, 5746 (1975); A. P. Murani (private communication).
- ³²N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. B 36, 2036 (1987).
- ³³O. Gunnarsson and K. Schönhammer, in *Theory of Heavy Fermions and Valence Fluctuations*, edited by T. Kasuya and T.

Saso (Springer-Verlag, Berlin, 1985), p. 110.

- ³⁴O. Gunnarsson and Schönhammer, Phys. Rev. B 40, 4160 (1989).
- ³⁵T. E. Scott, in *Handbook on the Physics and Chemistry of Rare Earths* (Ref. 2), Chap. 9, p. 701.
- ³⁶V. T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).
- ³⁷Reference 36 uses a different scaling energy, T_0 , which is proportional to T_K , $T_0 = (N/2\pi)T_K$.
- ³⁸J. W. Rasul and A. C. Hewson, J. Phys. C 17, 3337 (1984).
- ³⁹P. Schlottmann, Z. Phys. B 57, 23 (1984).
- ⁴⁰D. van der Marel, Ph.D. thesis, Groningen University, 1985; Narrow Band Phenomena—Influence of Electrons with Both Band and Localized Character, edited by J. C. Fuggle, G. A. Sawatzky, and J. W. Allen (Plenum, New York, 1988), p. 3.
- ⁴¹L. D. Landau and E. M. Lifshitz, *Statistical Mechanics* (Pergamon, London, 1958).
- ⁴²J. D. Thompson, Z. Fisk, J. Lawrence, J. L. Smith, and R. M. Martin, Phys. Rev. Lett. **50**, 1081 (1983).
- ⁴³D. Glötzel, J. Phys. F 8, L163 (1978).
- ⁴⁴W. E. Pickett, A. J. Freeman, and D. D. Koelling, Phys. Rev. B 23, 1266 (1981).
- ⁴⁵R. Podloucky and D. Glötzel, Phys. Rev. B 27, 3390 (1983).
- ⁴⁶B. I. Min, H. J. F. Jansen, T. Oguchi, and A. J. Freeman, Phys. Rev. B 34, 369 (1986).
- ⁴⁷O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B 41, 7311 (1990).
- ⁴⁸J. W. Allen, S.-J. Oh, O. Gunnarsson, K. Schönhammer, M. B. Maple, M. S. Torikachvili, and I. Lindau, Adv. Phys. 35, 275 (1985).
- ⁴⁹C. Laubschat, E. Weschke, C. Holtz, M. Domke, O. Strebel, and G. Kaindl, Phys. Rev. Lett. 65, 1639 (1990).
- ⁵⁰B. J. Beaudry and K. A. Gschneidner, Jr., in *Handbook on the Physics and Chemistry of Rare Earths* (Ref. 2), Chap. 2, p. 216.
- ⁵¹J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F 11, 121 (1981).
- ⁵²W. D. Schneider, B. Delley, E. Wuilloud, J.-M. Imer, and Y. Baer, Phys. Rev. B **32**, 6819 (1985).
- ⁵³G. Crecelius, G. K. Wertheim, and D. N. E. Buchanan, Phys. Rev. B 18, 6519 (1978).
- ⁵⁴D. M. Wieliczka, C. G. Olson, and D. W. Lynch, Phys. Rev. Lett. **52**, 2180 (1984).
- ⁵⁵For N = 2, J. R. Schrieffer and P. A. Wolff, Phys. Rev. 149, 491 (1966); for N > 2, B. Coqblin and J. R. Schrieffer, *ibid*. 185, 847 (1969).