Crystal-Field Splitting in Kondo Systems

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The mixing interaction in the Anderson model of local moments in metals $V_{\mathbf{k}\sigma,m}$ depends on the orbital state m of the local electron. We have taken into account this anisotropy and find that, quite aside from other mechanisms, e.g., crystalline electric fields, the mixing alone can account for the magnitudes of the splitting and linewidths of the local f states observed in Kondo-type systems, e.g., heavy-fermion and mixed-valence compounds.

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Our theoretical understanding of the behavior of Kondo-type systems is based on the Anderson model of local moments in metals. The central feature of this model is the mixing interaction between electrons in local and conduction states[1]

$$H_{\text{mix}}=\sum_{\mathbf{k}\sigma,m} V_{\mathbf{k}\sigma,m}c^{\dagger}_{\mathbf{k}\sigma}f_m+\text{H.c.}, \tag{1}$$

where

$$V_{\mathbf{k}\sigma,m}=\frac{1}{\sqrt{N_s}}\int \Psi^*_{jm}(\mathbf{r})V(\mathbf{r})\sum_{\mathbf{R}_i} e^{i\mathbf{k}\cdot\mathbf{R}_i}a_\sigma(\mathbf{r}-\mathbf{R}_i)d\mathbf{r}.$$

We have assumed the local state to be an f electron in a spin-orbit coupled j state, as we are interested in, *inter alia*, cerium compounds, and the conduction electron state is written in terms of Wannier functions. In the conventional treatment of the Kondo problem, only the isotropic part of the mixing interaction is considered, i.e., the dependence on the orbital index m in Eq. (1) is suppressed. This is justified as the central feature of the Kondo problem is the crossover from weak to strong coupling.

Here we show that the magnitude of the splitting due to the anisotropic component of the mixing interaction accounts for the "crystal-field" splittings observed in Kondo-type systems. The role of anisotropic mixing has been previously used to account for magnetocrystalline anisotropy in the cerium pnictides.[2] Kasuya showed that for these compounds there is near cancellation of the point charge and $5d$ screening contributions to the splittings of the $4f$ level; therefore, anisotropic mixing is the primary origin of these splittings. The new point we are making is that for Kondon systems the splittings due to anisotropic mixing, as well as the widths of the f levels, can be reliably estimated without recourse to band-structure calculations. We relate the "crystal-field" splittings to the *anisotropy* of the mixing interaction which we evaluate. The *overall scale* of the splittings is then fixed by the *isotropic* mixing parameter; this parameter has been previously found from studies of the isotropic spectra and thermodynamic behavior of Kondo-type systems.[3]

We start by summarizing the solution of the single-ion Anderson model in the Kondo regime when we take account of the anisotropy in the mixing interaction. We assume the mixing parameters $V_{\mathbf{k}\sigma,m}$ are weakly dependent on k and σ, and that mixing occurs with only one partial wave l of the conduction electron. By projecting the interaction onto a state $|m\rangle$ which is a linear combination of states $|jm_j\rangle$ which transform according to the irreducible representations of the point-group symmetry at the site of the local state, we write

$$V_{\mathbf{k}\sigma,m}=\begin{cases} f(\hat{\mathbf{k}}l\sigma,m)V_m, & -D<\epsilon_k<D \\ 0, & |\epsilon_k|>D, \end{cases} \tag{2}$$

where $f(\hat{\mathbf{k}}l\sigma,m)$ represents a combination of Clebsch-Gordan coefficients and spherical harmonics, and D is the half-width of the conduction band which will be assumed to be flat. We can use any of the $1/N$ expansion methods to solve the single-ion Anderson Hamiltonian[4]

$$H=\sum_{\mathbf{k}\sigma}\epsilon_k c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}+\sum_m \epsilon_{fm}f^{\dagger}_m f_m+U\sum_{m'>m} f^{\dagger}_{m'}f_{m'}f^{\dagger}_m f_m +\sum_{\mathbf{k}\sigma,m}V_{\mathbf{k}\sigma,m}c^{\dagger}_{\mathbf{k}\sigma}f_m+\text{H.c.}, \tag{3}$$

where we take the local state to have f $(l=3)$ character. Here ϵ_{fm} represents the splitting of the f electron energy by the *crystalline electric field*, e.g., the *Coulomb* interaction between the local f and the other electrons (conduction as well as those on ligand ions). It is not possible to make an *ab initio* estimate of this splitting in metallic systems; therefore, we set $\epsilon_{fm}\equiv\epsilon_f$, and focus on the splitting coming from the anisotropy of the *mixing* interaction.

We use the variational approach to obtain the ground state to first order in $1/N$, where $N=2j+1$ is the degeneracy of the local state; $N=6$ for cerium $j=\frac{5}{2}$. By using this procedure at $T=0$ K we find the ground-state energy for this many-body system in the limit of infinite U is given as[4,5]

$$E_0=\sum_{km}^{\text{occ}}\frac{|V_m|^2}{E_0-\epsilon_f+\epsilon_k-\Sigma_m(E_0+\epsilon_k)}, \tag{4a}$$

where

$$\Sigma_m(z) = |V_m|^2 \sum_k^{\text{unocc}} \frac{1}{z-\epsilon_k-\Sigma_0(z-\epsilon_k)} \tag{4b}$$

is the self-energy of the f^1 configuration, and

$$\Sigma_0(z) = \sum_{km}^{\text{occ}} \frac{|V_m|^2}{z-\epsilon_f+\epsilon_k-\Sigma_m(z+\epsilon_k)} \tag{4c}$$

is the self-energy of the f^0 configuration. For a flat density of conduction-electron states of half-width D, we find

$$E_0 \approx \frac{1}{\pi}\sum_m \Gamma_m \ln\left|\frac{E_0-\epsilon_f-\Sigma_m(\epsilon_f)}{D}\right| , \tag{5a}$$

$$\Sigma_m(\epsilon_f) \approx \frac{\Gamma_m}{\pi}\ln\left|\frac{\epsilon_f-D}{\epsilon_f}\right| , \tag{5b}$$

$$\Sigma_0(z) = \frac{1}{\pi}\sum_m \Gamma_m \ln\left|\frac{z-\epsilon_f-\Sigma_m(z)}{D}\right| , \tag{5c}$$

where we defined

$$\Gamma_m \equiv \pi N(0)\,|V_m|^2 , \tag{6}$$

and $N(0)$ is the single-particle density of states.[3,4] The many-body ground-state energy is found from Eq. (5a) to be

$$E_0 = \epsilon_f + \min[\Sigma_m(\epsilon_f) - T_m] , \tag{7}$$

where T_m is the solution of the equation

$$\epsilon-\epsilon_m+\frac{1}{\pi}\sum_{m'}\Gamma_{m'}\ln\left|\frac{\Sigma_m(\epsilon_f)-\Sigma_{m'}(\epsilon_f)-\epsilon}{D}\right| = 0 ,$$

i.e.,

$$T_m \approx \frac{De^{-\pi|\epsilon_m|/N_m\Gamma_m}}{\prod_{m'\neq m}|[\Sigma_m(\epsilon_f)-\Sigma_{m'}(\epsilon_f)-T_m]/D|^{N_{m'}\Gamma_{m'}/N_m\Gamma_m}} , \tag{8a}$$

where

$$\epsilon_m \equiv \epsilon_f + \Sigma_m(\epsilon_f) ,$$

and N_m is the degeneracy of the mth sublevel. For a two-level system this result reduces to that found by Yamada, Yosida, and Hanzawa.[6]

From above solution we identify the following:

(1) The splitting of the local f state

$$\Delta_{mn} \equiv \Sigma_m(\epsilon_f) - \Sigma_n(\epsilon_f) = \frac{1}{\pi}(\Gamma_m-\Gamma_n)\ln\left|\frac{\epsilon_f-D}{\epsilon_f}\right| . \tag{9}$$

(2) The shift of the center of the f levels

$$\Delta_0 = \frac{1}{N}\sum_m \Sigma_m(\epsilon_f) = \frac{\Gamma}{\pi}\ln\left|\frac{\epsilon_f-D}{\epsilon_f}\right| , \tag{10}$$

where we relate the sum $\sum_m \Gamma_m \equiv N\Gamma$ to the *isotropic* mixing parameter Γ.

(3) The width of the f levels, which are estimated from the imaginary part of Eq. (4b) to be,

$$\begin{aligned}\Gamma_m^* &\equiv \operatorname{Im}\Sigma_m(\epsilon_f)\\ &= \operatorname{Im}|V_m|^2\sum_k^{\text{unocc}}\frac{1}{z-\epsilon_k-\Sigma_0(z-\epsilon_k)}\bigg|_{z=\epsilon_m+i0^+}\\ &= \Gamma_m\left[\frac{d}{d\epsilon}\left(\epsilon-\epsilon_m+\frac{1}{\pi}\sum_{m'}\Gamma_{m'}\ln\left|\frac{\Sigma_m-\Sigma_{m'}-\epsilon}{D}\right|\right)\bigg|_{\epsilon=T_m}\right]^{-1} ,\end{aligned} \tag{11}$$

we find

$$\Gamma_m^* \approx \frac{\pi\Gamma_m}{\sum_{m'}[N_{m'}\Gamma_{m'}/(T_m-\Delta_{mm'})]} = \frac{\pi T_m}{N_m}\left[1+\sum_{m'\neq m}\frac{N_{m'}\Gamma_{m'}/N_m\Gamma_m}{1-\Delta_{mm'}/T_m}\right]^{-1} . \tag{12}$$

This linewidth can be written in terms of the conventional low-temperature energy scale for the Kondo problem.[3,4]

$$T_0 \approx De^{-\pi|\epsilon_f|/N\Gamma} . \tag{13}$$

By comparing Eqs. (9) and (12), we find that the widths of the "crystal-field" levels are smaller than the splittings by $\pi T_m/N_m\Gamma_m$ which is just the renormalization constant Z when we take into account the anisotropy of the mixing parameter. For the Kondo regime of the Anderson model, Z is quite small. From Eqs. (9) and (10) we note that the overall energy scale for the local states splittings is that of the isotropic parameter Γ; this is typically of the order of 15 to 20 meV for Kondo-type alloys containing cerium. This implies that the half-width of the Friedel-Anderson resonance $\Delta = N\Gamma$ is about 0.1 eV. On the contrary, the scale for the linewidths is given by T_0; this is of the order of 1 meV.

To determine the anisotropy of the mixing interaction we have evaluated the two-center integrals entering the mixing parameters V_m of Eq. (1) in terms of *one* parameter that is related to the conventional isotropic parameter Γ. To keep the number of parameters to a minimum we made the following assumptions: (1) The Wannier function in Eq. (1) is replaced by an atomic orbital with a definite angular momentum. For example, for copperbased compounds we consider s orbitals, while for aluminum compounds, p orbitals. (2) There is no simple expression for the mixing interaction $V(\mathbf{r})$ in Eq. (1)[7]; we consider it to be a function only of its radial variable. With these two assumptions the two-center integral in the mixing interaction separates into a product of Slater-Koster (SK) integrals, and angular variables.[2,8] When we sum the contributions from equivalent anion sites we use angular momentum rotation matrices to refer the angular variables to a common set of axes; the SK integrals are the same for all equivalent sites. When these are more than one set of equivalent anion neighbors we introduce a different set of SK integrals for each set.

To evaluate the two-center integrals and to sum over the neighboring anion sites, we used the Slater-Koster tables for f electrons developed by Takegahara, Aoki, and Yanase.[8] We write the V_m in terms of SK integrals which are treated as unknown parameters. By expressing the isotropic mixing parameter

$$\Gamma=\frac{1}{N}\sum_m \Gamma_m=\pi\frac{N(0)}{N}\sum_m |V_m|^2 \tag{14}$$

in terms of these SK integrals we obtain the sought-after relation that provides the overall energy scale of the anisotropic mixing parameters. For those situations when more than one SK integral enters V_m, i.e., when there is more than one set of equivalent neighbors or when the atomic orbitals on the anion sites have p or higher angular momentum, we make additional assumptions to eliminate the unknown parameters.

As examples of the above method we considered $CeAl_2$ and $CeAl_3$. $CeAl_2$ has a cubic structure where cerium is surrounded by twelve equivalent aluminum neighbors.[9] For this case we must introduce two SK integrals σ and π depending on whether the aluminum p orbital is pointing towards or normal to the central cerium ion. In cubic symmetry, the six states $|j=\frac{5}{2},m_j\rangle$ can be rewritten as linear combinations which transform according to the irreducible representations Γ_7 and Γ_8. After summing over the neighboring ions we find

$$|V_{\Gamma_7}|^2=0.225\sigma^2+0.440\pi^2 \tag{15}$$

and

$$|V_{\Gamma_8}|^2=0.317\sigma^2+0.374\pi^2 .$$

The splitting of the local $4f$ state in $CeAl_2$, see Eq. (9), is

$$\Delta_{87}=(0.092\sigma^2-0.066\pi^2)N(0)\ln\left|\frac{\epsilon_f-D}{\epsilon_f}\right|, \tag{16a}$$

while the isotropic mixing parameter Eq. (14) is given as

$$\Gamma=(0.286\sigma^2+0.396\pi^2)\pi N(0) . \tag{17}$$

The same combination of σ and π does not enter the splitting and isotropic shift; therefore, we made the reasonable assumption that $\pi^2 \ll \sigma^2$.[10] By placing Eq. (17) in (16), we find the Γ_7-Γ_8 splitting is

$$\Delta_{87}=\frac{0.32}{\pi}\Gamma\ln\left|\frac{\epsilon_f-D}{\epsilon_f}\right| . \tag{16b}$$

To determine the splitting we used a set of parameters that has been found to give a good description of the isotropic behavior of Kondo systems containing, cerium,[3] i.e., for $N=6$, $\epsilon_f/D=-0.67$, $\Gamma/D=0.05$, and $D=3$ eV; this is the parameter set No. 1 in Table I of Ref. 3. For $CeAl_2$, we find

$$\Gamma_{87}=162\text{ K} . \tag{18}$$

This value compares quite favorably with the data found from neutron scattering experiments on $CeAl_2$,[11] i.e., a Γ_7 ground state with $\Delta_{87}\approx 100$ K.

The widths of the levels are estimated from Eqs. (8a) and (12). By using Eqs. (9), (13), (15), and (17) we find the characteristic low-temperature energy scale T_m for a two sublevel system is written as

$$T_m=\left|\frac{T_0}{\Delta_{mm'}-T_m}\right|^{N_{m'}\Gamma_{m'}/N_m\Gamma_m} T_0 . \tag{8b}$$

By using the observed splitting Δ_{87}, and the T_0 found from Eq. (13) when the above parameters are used we find

$$\Gamma_7^*=2\text{ K}$$

and

$$\Gamma_8^*=21\text{ K} . \tag{19}$$

These values are close to these observed[11,12] $\Gamma_7^*\approx 3$–5 K and $\Gamma_8\approx 20$ K.

$CeAl_3$ has a hexagonal Ni_3-type structure for which the cerium $j=\frac{5}{2}$ level is split into three doublets.[13] There are sixteen neighboring aluminum ions around the cerium. Six are in a plane containing the cerium, five in a plane above, and another five in a plane below. As there are two inequivalent sets of aluminum ions we have four SK integrals. We made the same assumption as for $CeAl_2$ that $\pi^2\ll\sigma^2$, and we fix the ratio of the SK σ integrals in and out of the plane to reproduce the observed ratio of the splittings between the doublets. We find $\sigma_{\text{out}}/\sigma_{\text{in}}=0.77$ which is entirely reasonable. In a manner analogous to our calculations above we find for $CeAl_3$

$$\Delta_{21}=\frac{0.27}{\pi}\Gamma\ln\left|\frac{\epsilon_f-D}{\epsilon_f}\right|$$

and

$$\Delta_{31}=\frac{0.39}{\pi}\Gamma\ln\left|\frac{\epsilon_f-D}{\epsilon_f}\right|, \tag{20}$$

where Δ_{21} is the splitting between the ground and first excited doublet and Δ_{31} is between the ground and second excited doublet. By using the *same* parameter set as before we find

$$\Delta_{21}=137\ \mathrm{K}\,,\qquad \Delta_{31}=198\ \mathrm{K}\,. \tag{21}$$

Again these values compare favorably (see discussion below) with the data on CeAl$_3$,[14] i.e., $\Delta_{21}\approx 60$ K, and $\Delta_{31}\approx 88$ K. By using the observed splittings Δ_{21} and Δ_{31} and the T_0 from Eq. (13) we find from Eq. (12) the linewidths are

$$\Gamma_1^*=4.5\ \mathrm{K}\,,\qquad \Gamma_2^*=25\ \mathrm{K}\,,\qquad \Gamma_3^*=26\ \mathrm{K}\,. \tag{22}$$

These values are close to those observed[14] $\Gamma_1^*\approx 5$ K, and $\Gamma_2^*\approx\Gamma_3^*\approx 23$ K.

We note the estimated splittings for both CeAl$_2$ and CeAl$_3$ are larger than those observed. This is understandable when one realizes that the orbitals on the anion (aluminum) sites are more diffuse than the atomic orbitals used in our calculations. As the orbitals spread out the anisotropic component of the mixing decreases, i.e., they eventually form a spherelike charge distribution which is isotropic. On the other hand, our estimates of the linewidths should be close to those observed because we used the actual splittings $\Delta_{mm'}$.

In conclusion, we can account for the "crystal-field" splittings of local states in Kondo-type systems without introducing new interactions or parameters in the Anderson model. From our examples we find anisotropic mixing alone can account for the magnitudes of the splittings and linewidths of the local $4f$ states observed in Kondo-type cerium compounds. Indubitably, there are other contributions to the "crystal-field" splittings, i.e., the $\epsilon_{fm}\neq\epsilon_f$ in Eq. (3). We are unable *a priori* to estimate these splittings; however, *a posteriori* we can infer that their *net* effect is small compared to the splitting coming from the mixing interaction. From Eqs. (9), (16), and (20) we note that the *scale* of the splittings is governed by the isotropic mixing parameter Γ, while the actual size depends on the anisotropy of the Γ_m-Γ_n mixing. The scale of the linewidths of the levels Eqs. (8b) and (12) is given by the temperature T_0, however, the linewidths are also proportional to Γ_m. For certain symmetries this is anomalously small, viz., $V_{\Gamma_7}=0$ when the local electron is surrounded by an octahedron of anions.

While we have presented results on cerium compounds we are presently extending our study to other rare-earth and actinide (uranium) compounds. In the future, we will present the results of our calculations of the anisotropy of the thermodynamic and transport properties of Kondo-type compounds due to the anisotropy of the mixing interaction.

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