Theory for the Anomalous Hall Constant of Mixed-Valence Systems

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We show that the large anomalous Hall constants of mixed-valence and Kondo-lattice systems can be understood in terms of a simple resonant-level Fermi-liquid model. Splitting of a narrow, orbitally unquenched, spin-orbit split, f resonance in a magnetic field leads to strong skew scattering of band electrons. We interpret both the anomalous signs and the strong temperature dependence of Hall mobilities in $CeCu_2Si_2$, SmB_6, and $CePd_3$ in terms of this theory.

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Anomalous transport properties are a characteristic feature of mixed-valence (MV) or Kondo-lattice compounds.[1] One of the first and most striking aspects of these transport properties to be observed was the anomalous Hall constant.[2] In three systems so far studied, SmB_6,[3] $CePd_3$,[4] and the heavy-fermion metal $CeCu_2Si_2$,[5] very large Hall constants have been observed, at least 100 times larger than in normal metals, with anomalous positive signs.

The relevant parameter measuring the anomalous transverse scattering of electrons is the Hall mobility μ_H (=Hall constant/resistivity). Figure 1 compares the Hall mobilities of SmB_6, $CePd_3$, and $CeCu_2Si_2$. The Hall mobilities of SmB_6 and $CePd_3$ show a marked resemblance, increasing from a large negative value at low temperatures to become positive at high temperatures. This similarity is particularly striking because SmB_6 becomes an insulator at low temperatures, while $CePd_3$ is metallic. These comparable Hall mobilities indicate similar skew-scattering mechanisms operating independently of the coherent effects of band formation in both materials. We will show that this provides one of the most direct pieces of evidence that we have for the local character of the scattering mechanism in these systems, adding new support for the local Fermi-liquid picture of mixed valence.[6] $CeCu_2Si_2$ has a positive Hall mobility which rises by a factor of about 20 below 20 K. Aliev *et al.*[5] interpreted this effect as a result of the growth of a many-body resonance at low temperatures, but they provided no mechanism to explain how this affects the Hall mobility.

Here we present a simple model which appeals to the Fermi-liquid properties of the MV ground state to explain these anomalies. From renormalization-group analysis and exact solution[7-9] we know that the low-energy thermodynamics and scattering of a MV ion are described by a resonance level (RL) of width Δ^* at a position E_f^* above the Fermi energy. The RL describes a renormalized f state with $2j+1=N$ degenerate scattering channels, each characterized by an azimuthal quantum number m_j.[6,10] Both Δ^* and E_f^* are related to the bare quantities Δ and E_f of the corresponding noninteracting state. In the MV regime where $E_f > -N\Delta$, $\Delta^* \approx \Delta$, while in the Kondo regime where $E_f < -N\Delta$, Δ^* is strongly renormalized down to the Kondo temperature $\Delta^* \approx D\exp(\pi E_f/N\Delta)$, where $2D$ is the bandwidth. Friedel's sum rule constrains the $2j+1=N$ scattering phase shifts $\delta_3(\omega)$ of the f channel at the Fermi energy μ, $\delta_3(\mu) = \tan^{-1}(\Delta^*/E_f^*)$, to sum to the local f charge $N\delta_3(\mu)/\pi = n_f$, which fixes E_f^*. In our model we assume that the spin-orbit splitting between the $j=\frac{5}{2}$ and $j=\frac{7}{2}$ levels is far larger than Δ^* so that the δ^3 are

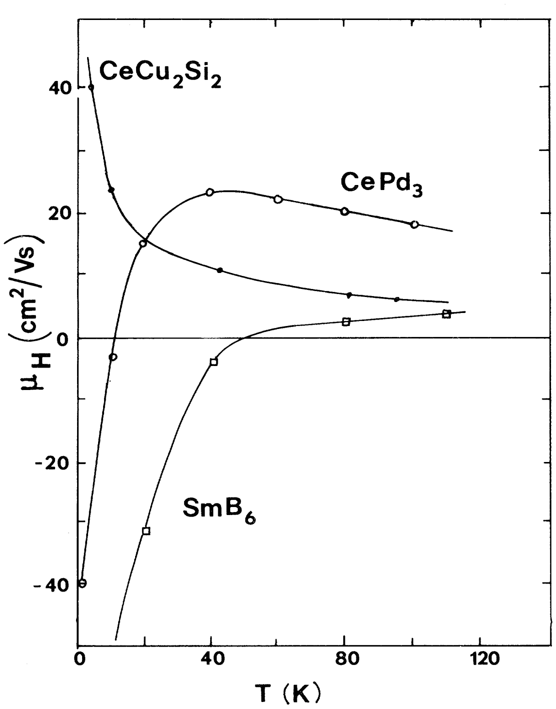

FIG. 1. Hall mobilities of $CeCu_2Si_2$, $CePd_3$, and SmB_6.

only large in one of the two j states.

We shall model a dense MV or Kondo-lattice system as a lattice of RL's. Theoretical arguments show that the nonlocal correlations in the dense Fermi liquid are of order $1/N$ ($=\frac{1}{6}$ for Ce),[10] but clearly the attraction of this model is its simplicity. Heavy-band formation arises naturally through the coherent scattering action of the RL's, but throughout this paper we neglect these coherence effects and hence our results should not apply to the lowest temperatures where the heavy band is well developed.

If a magnetic field B is applied, the degeneracy of the f-level positions is split according to $E_{fm}^* = E_f^* + (g\mu_B)B$, where $g\mu_B$ is the moment of the f state. This modifies the f-channel phase shifts, $\delta_{3m}(\mu) = \delta_3(\omega - mg\mu_B B)$, by shifting the RL's. In a weak field

$$\delta_{3m}(\mu) = \delta_3(\omega) - mg\mu_B B\, \partial\delta_3/\partial\omega + O(B^2). \tag{1}$$

The field-dependent component in the scattering t matrix is then given by

$$\delta\hat{t}(\omega) = (g\mu_B/\rho)\alpha(\omega)\mathbf{J}\cdot\mathbf{B}, \tag{2}$$

where ρ is the band electron density of states and $\alpha(\omega) = \exp(2i\delta_3)\partial\delta_3/\partial\omega$. Now $(N/\pi)\partial\delta_3/\partial\omega = \rho_f$ is the f-quasiparticle density of states, i.e., $1/T_K$ in the Kondo regime. Thus α is very large because a small splitting of the narrow Kondo resonance leads to a large change in the phase shifts. This creates a large amount of skew scattering. Within the RL model, ρ_f can be related to the magnetic susceptibility $\chi(T)$ by $\rho_f = \tilde{\chi}(0)$, where $\chi = \frac{1}{3}(g\mu_B)^2 J(J+1)\tilde{\chi}$,[6] so that large skew scattering accompanies high susceptibilities.

Now at high temperatures one can use perturbation theory and the Anderson model for the impurity to derive the t matrix,

$$t_m(\mu) \approx -K(T)(1-n_{fm}), \tag{3}$$

where $K(T) = -V^2/E_f(T)$ and

$$E_f(T) \approx E_f + N(\Delta/\pi)\ln(D/T)$$

is the temperature-dependent renormalized f-level position[9] and n_{fm} is the average occupation of the f state in the mth f channel. In a magnetic field $\partial n_{fm}/\partial B \approx -\pi\tilde{\chi}/N$ so that the field-dependent part of t_m has the same form as Eq. (2) but with $\alpha \approx -pK(T)\tilde{\chi}/N$. In the Kondo regime, $K(T)$ is related[8] to $\tilde{\chi}$ via $[1-\rho K(T)]/T \approx \tilde{\chi}(T)$ so that $\alpha(T) \approx -\tilde{\chi}(1-\tilde{\chi}T)/N$, enabling us to summarize the scattering at high and low temperatures by writing $\alpha(T) = |\alpha(T)|e^{-i\phi(T)}$, where

$$\begin{aligned} &\phi(T) = -2\delta_3, \quad |\alpha| \sim \tilde{\chi}/N, \quad T \ll \Delta^*, \\ &\phi(T) = -\pi, \quad |\alpha| \sim \tilde{\chi}(1-\tilde{\chi}T)/N, \quad T \gg \Delta^*. \end{aligned} \tag{4}$$

There is clearly a large drop in $|\alpha|$ from $1/T_K$ to $\rho K/T \ll 1/T$ as the temperature rise from 0 K to above T_K. Perhaps most interesting is the change in the phase ϕ which occurs as a consequence of the temperature-dependent renormalization of the f level, where at high temperatures it scatters with phase shift $\approx \pi$ from each occupied f channel. Similar results hold in the MV regime with T_K replaced by $\Delta^* \sim \Delta$ and $\rho K \sim 1$.

We now discuss how this field-dependent scattering affects the Hall constant. To be specific we consider a cerium ion with $J = \frac{5}{2}$. The field-dependent t matrix is conveniently written in a spin and momentum representation by use of the result

$$\langle \mathbf{k}\sigma | \mathscr{P}_{j=5/2}\mathbf{J}\cdot\mathbf{B} | \mathbf{k}'\sigma' \rangle = -(5i/\pi)[1 + P_2(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')](\hat{\mathbf{k}}\times\hat{\mathbf{k}}')\cdot\mathbf{B} + S_{\sigma\sigma'}T_{\text{flip}}. \tag{5}$$

$\mathscr{P}_{j=5/2}$ projects states into the $l=3$, $j=\frac{5}{2}$ subspace of the f level. The spin-flip term leads to a Hall current of $O(B^2)$ and will be neglected. Substituting (5) into (2) and including potential scattering in the other angular momentum channels, in particular $l=2$, we find that the scattering probability $|t_{\mathbf{kk}'}|^2$ has the form

$$|t_{\mathbf{kk}'}|^2 = |t^0_{\mathbf{kk}'}|^2 + \mathbf{B}\cdot(\hat{\mathbf{k}}\times\hat{\mathbf{k}}')\,W_s(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}') + O(B^2), \tag{6}$$

where $t^0_{\mathbf{kk}'}$ is the zero-field component of the t matrix. The second term results from interference between the zero-field $l=2$ and strongly field-dependent $l=3$ terms. $W_s(\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')$ leads to a skew-scattering rate of the band electrons given by[11,12]

$$\Gamma_s(\omega) = 2\pi\rho B\int_{-1}^{1} d\cos\theta\,(2\pi/3)\,W_s(\cos\theta,\omega)[1-P_2(\cos\theta)], \tag{7}$$

and the Hall constant is related simply to Γ_s by[11,12]

$$\delta R_H = (1/\mathscr{N}e)(m/\mathscr{N}e^2)\langle\Gamma_s(\mu)\rangle/B. \tag{8}$$

Here $\mathscr{N}$ is the band electron density, $\Gamma_s = -\int(\partial f/\partial\omega)\Gamma_s(\omega)d\omega$ is a thermal average of $\Gamma_s(\omega)$ about the Fermi energy μ, and $f(\omega)$ is the Fermi function. For $T \ll \Delta^*$ and $T \gg \Delta^*$ we can write $\langle\Gamma_s(\mu)\rangle \approx \Gamma_s(\mu)$. With an $l=2$ phase shift δ_2 and a corresponding scattering rate

$$1/\tau_2 = \tfrac{6}{7}n_i[(4\pi/k_F)^2 v_F 5\sin^2\delta_2],$$

where n_i is the concentration of the MV ions, we then find that

$$\delta R_{\mathrm{H}} = \rho_2 (g\mu_{\mathrm{B}}) |\alpha| \{\sin(\phi - \delta_2)/\sin\delta_2\}, \quad (9)$$

where $\rho_2 = m/Ne^2\tau_2$. The last part of this expression results from interference between the d and f channels. This term determines the sign of the Hall anomaly. For $T >> \Delta^*$, $\phi \approx -\pi$ so that δR_{H} is positive. At low temperatures, $\phi = -2\delta_3 = -(2\pi/N)n_f$ so that

$$\delta R_{\mathrm{H}} \propto -\sin(2n_f/N + \delta_2)/\sin\delta_2$$

can have either sign.

In earlier theories for the anomalous Hall effect[11-13] a weak spin-orbit coupling λ generates the skew scattering. Since λ is weaker than the crystal-field splitting, the orbital moments are quenched and magnetization is solely due to the electron spin. We have considered the opposite extreme where λ is much larger than the crystal-field splitting, insuring unquenched orbital moments, so that our mechanism for anomalous Hall scattering differs completely from the weak spin-orbit effect considered previously. The other major difference is the modeling of a rather complicated MV ground state by an effective resonance level rather than the literal resonant-level model of Fert and Jaoul.[11]

In a dense RL lattice the anomalous scattering off each of the RL's is essentially that of a single impurity, and so the Hall mobility $\mu_{\mathrm{H}} = R_{\mathrm{H}}/\rho_{\mathrm{imp}}$ should have the same behavior in the bulk as for the impurity. The bulk anomalous Hall constant should therefore be

$$\delta R_{\mathrm{H}} \sim \rho_{\mathrm{bulk}} (g\mu_B) \alpha(T) \times \{\sin[\phi(T) - \delta_2]/\sin\delta_2\}. \quad (10)$$

A striking illustration of the essential correctness of this picture is provided by comparing the Hall effect in SmB_6 with that of $CePd_3$. In SmB_6, lattice coherence leads to a small semiconducting gap and resistivity rises through three decades as the temperature is lowered.[3] In relatively clean metallic $CePd_3$, the resistivity drops with the temperature.[4] Despite this, the Hall mobilities behave similarly in respect to temperature dependence and size.

When we include in addition the effects of real crystal electric fields, the locally degenerate states are split, increasing the phase shifts to satisfy the sum rules. This can change the sign of the interference term and the Hall effect. Spin-orbit coupling is an order of magnitude larger than crystal fields in rare-earth metals and its role in stabilizing the f-orbital moments is vital at this point. We have not calculated R_{H} with crystal fields, where the t matrix has the appropriate reduced symmetry. However, there will still be terms proportional to $L_z B_z$ (B_z along the appropriate crystal axis) with considerable anisotropy in scattering. Thus we can still make a comparison with real systems.

For $CeCu_2Si_2$, neutron scattering indicates that the Kondo resonance is a Kramers doublet[14] with the next excited crystal-field doublet state lying ~ 140 K above the ground state. The positive R_{H} at all temperatures $T \leqslant 140$ K can be attributed to a twofold-degenerate system which at low temperatures gives a phase shift of $\delta_3 \approx \pi/2$, giving $R_{\mathrm{H}} > 0$ by (10). Using known parameters for $CeCu_2Si_2$, $\rho_{\mathrm{bulk}}(T=0) \approx 80$ $\mu\Omega$ cm, $g_{\mathrm{eff}} \approx 2.0$ (from crystal-field parameters), $\chi \approx 0.08$ emu/mol, we find that $\alpha^{-1} \approx 80$ K and hence $R_{\mathrm{H}} \sim 10^{-2}$ $\mathrm{cm^3/C}$, in reasonable agreement with the quoted results $R_{\mathrm{H}} \approx 4 \times 10^{-2}$ $\mathrm{cm^3/C}$.[5] The temperature dependence of R_{H} also matches the form

$$R_{\mathrm{H}} \sim \chi(T)[1 - T\tilde{\chi}(T)/\lim_{T\to\infty} T\chi(T)]$$

reasonably well, although the observed decrease is slower above 100 K (Fig. 2).

Both $CePd_3$ and SmB_6 have no observed crystal-field splitting, suggesting that the full sixfold degeneracy is involved in formation of the mixed-valence ground state. In $CePd_3$ the resistance and susceptibility maxima at $T \sim 100$ K suggest a scattering resonance positioned ~ 100 K above the Fermi energy, which corresponds to a $\Delta^* \sim 50$ K for the assumptions $N = 6$ and $n_f \sim 1$. The high-temperature Hall coefficient is positive and tracks roughly with the susceptibility, as expected from the incoherent skew scattering [Eq. (4)]. At low temperatures $T << \Delta^* \sim 50$ K, we expect ϕ to renormalize from $\phi = -\pi$ to $-2\delta_3 = -\pi n_f/3 \sim -\pi/3$. It is tempting to ascribe the change in sign of R_{H} to a change in sign of the interference term due to the passage of $\phi + \delta_2$ through zero, though clearly band-formation effects may also play an important role below 10 K. The behavior of SmB_6 can be interpreted similarly, regarding μ_{H} as a measure of local skew scattering as already discussed.

We expect large anomalous Hall constants to occur

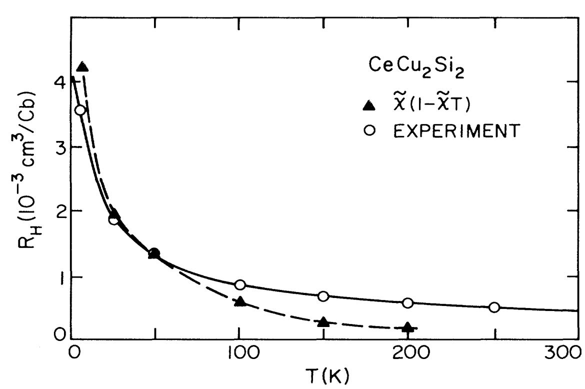

FIG. 2. $R_{\mathrm{H}}(T)$ for $CeCu_2Si_2$ compared with the approximate relation $R_{\mathrm{H}}(T) \sim \chi(T)[1 - T\tilde{\chi}(T)/\lim_{T\to\infty} T\chi(T)]$.

generally in the MV lanthanide and heavy-fermion actinide systems where the almost localized f electrons form narrow quasiparticle bands with extreme sensitivity to a magnetic field. The sign and magnitudes of these Hall anomalies provide important new information about the heavy-fermion ground state. This is a sparsely investigated aspect of mixed valence and deserves more experimental attention.

At the very lowest temperatures in very pure compounds, true heavy bands will be formed. In this regime the current carried by each Bloch state will have a skew component differing widely between different Fermi-surface regions, so that the resultant Hall effect can only be derived from a detailed band structure and transport theory. We do not speculate on this $T \rightarrow 0$ Fermi-liquid limit.

Finally, we note that this mechanism can explain long-standing Hall anomalies in two other classes of systems. Many rare-earth metals, and incidentally, also uranium, have positive Hall anomalies at high temperatures in solid and molten states.[15] Further afield, many Pauli paramagnetic metallic glasses[16] containing transition metals have positive Hall constants. One may speculate that the short electronic mean free paths and lack of crystalline order suppresses any crystal-field quenching of orbital angular momentum so that the above mechanism can operate.

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