thank J. S. Faulkner for helpful discussions.

*Work supported mainly by the U. S. Atomic Energy Commission through Contract No. AT(11-1)-3161.

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Crystal-Field Effect on a Kondo System: Magnetic Susceptibility of La:Ce†

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In this paper we evaluate the effect of the cubic crystalline field on the magnetic susceptibility of the Kondo system La:Ce. We show the coexistence of the crystal-field splitting and the Kondo effect whenever the crystal field does not remove the degeneracy of the localized states completely. The theoretical curve is in good agreement with the experimental data for a choice of the Kondo temperature $T_K = 0.1$ K.

Recently there has been considerable work on low-temperature properties of cubic La:Ce. It is now well established that the La:Ce system behaves as a Kondo system. On the other hand, some uncertainty exists concerning the value of T_K, the Kondo temperature of the system. From resistivity measurements on La:Ce, Kim and Maple,[1] Gey and Umlauf,[2] Sugawara and Eguchi,[3] and Wollan and Finnemore[4] find the Kondo temperature T_K to be less than 1 K; similarly, from nuclear orientation studies Flouquet[5] finds a Kondo temperature T_K of about 0.1 K, while Edelstein and co-workers[6,7] from susceptibility measurements estimate T_K to be about 20 K.[8] Edelstein[7] analyzes experimental results using a phenomenological density of states for La:Ce. On the other hand, his tentative analysis in terms of a crystal field only[6] fails just in the low-temperature region.

Evidence for the coexistence of the crystal-field splitting and the Kondo effect has been found by Yoshida and Sugawara[9,10] in single crystals of Y:Ce. Others,[11-13] taking into account crystal-field splitting, showed the presence of sidebands in the resistivity of a Kondo system. A recent analysis of the crystal-field effect on the resistivity has been made by Cornut and Coqblin,[14] using the Schrieffer-Wolff transformation in the framework of the Anderson model, and by the present authors[15] using the s-f exchange Hamiltonian. In this paper we calculate the magnetic susceptibility of the Kondo system La:Ce in the cubic phase, taking into account both crystal-field effects and the coupling between the local spin J and the conduction-electron spin s. The exchange interaction is conventionally written as $H_{sf} = -\Gamma \vec{J}\cdot\vec{s}$. Though the s-f exchange Hamiltonian has not had first-principles justification except when it can be derived from the Anderson Hamiltonian, it has been used extensively. Cornut and Coqblin[14] find that applying the Schrieffer-Wolff transformation to the Anderson model leads to a Hamiltonian which is different than H_{sf}. We use H_{sf} for simplicity since it is still not completely clear which is the correct Hamiltonian. The use of this Hamiltonian appears to be well suited to the La:Ce case.[15,16]

Separate contributions to the magnetic susceptibility from crystal-field and s-d (or s-f) interactions were calculated respectively by Murao

and Matsubara[17] and by Miwa[18] (see also Yosida and Okiji[19]). The complete Hamiltonian is

$$H = H_{fe} + H_{cf} + H_{sf}, \tag{1}$$

where H_{fe} is the free-electron Hamiltonian and H_{cf} the cubic crystal-field Hamiltonian (see Ref. 17 for further details). We assume that the g value of the conduction electrons is zero.[20] The susceptibility is then calculated with the formula[21]

$$\chi = (g\mu_B)^2 \int_0^\beta d\lambda \langle e^{\lambda H} J_z e^{-\lambda H} J_z \rangle, \tag{2}$$

where $\beta = 1/k_B T$ and

$$\langle O \rangle \equiv \mathrm{Tr}(O e^{-\beta H})/\mathrm{Tr}(e^{-\beta H}). \tag{3}$$

We expand the ordered exponentials in Eq. (2) up to second order in Γ:

$$e^{-\lambda H} = e^{-\lambda H_0}[1 - \int_0^\lambda du_1 H_{sf}(u_1) + \iint_{\lambda > u_1 > u_2 > 0} du_1 du_2 H_{sf}(u_1) H_{sf}(u_2) - \cdots], \tag{4}$$

where $H_0 = H_{fe} + H_{cf}$ and $H_{sf}(u) = \exp(uH_0) H_{sf} \exp(-uH_0)$. This perturbative approach in the s-f interaction should give reliable results for $T > T_K$.

Owing to the noncommutativity of H_{cf}, H_{sf}, and J_z, the result, which we obtain by rearranging various terms, is not so simple as in Miwa's calculation. The lowest-order term is

$$\chi^{(0)} = (g\mu_B)^2 \int_0^\beta d\lambda \langle J_z(\lambda) J_z \rangle_0, \tag{5}$$

where $J_z(\lambda) = \exp(\lambda H_{cf}) J_z \exp(-\lambda H_{cf})$ and $\langle \cdots \rangle_0$ denotes a thermal average for the system in the absence of the s-f interaction. The next nonvanishing terms which are second order in Γ are

$$\chi_A^{(2)} = (g\mu_B)^2 \int_0^\beta d\lambda \int_0^\lambda du_1 \int_\lambda^\beta du_2 \langle H_{sf}(u_2)[J_z(\lambda), H_{sf}(u_1)] J_z \rangle_0, \tag{6}$$

$$\chi_B^{(2)} = (g\mu_B)^2 \int_0^\beta d\lambda \int_0^\lambda du_1 \int_0^{u_1} du_2 \langle [J_z(\lambda), H_{sf}(u_1) H_{sf}(u_2)] J_z \rangle_0, \tag{7}$$

$$\chi_C^{(2)} = (g\mu_B)^2 \int_0^\beta d\lambda \int_0^\beta du_1 \int_0^{u_1} du_2 \langle H_{sf}(u_1) H_{sf}(u_2) J_z(\lambda) J_z \rangle_0, \tag{8}$$

$$\chi_D^{(2)} = -(g\mu_B)^2 \int_0^\beta d\lambda \langle J_z(\lambda) J_z \rangle_0 \int_0^\beta du_1 \int_0^{u_1} du_2 \langle H_{sf}(u_1) H_{sf}(u_2) \rangle_0. \tag{9}$$

We note that $\chi^{(0)}$ simply gives the crystal-field contribution as obtained by Murao and Matsubara.[17] On the other hand, $\chi_A^{(2)}$ goes to Miwa's result in the limit $H_{cf} \to 0$ (the other $\chi^{(2)}$ terms giving zero contribution in this limit). Now we want to evaluate these various contributions for the La:Ce system.

As the spin-orbit coupling is strong in cerium, the ground state, $^2F_{5/2}$, and the next excited, $^2F_{7/2}$, are very distant in energy (about 2200 cm^{-1}). For these reasons at ordinary temperature one can regard $J^2 = \mathrm{const}$ and limit oneself to the subspace with $J = \frac{5}{2}$.

In a cubic crystal field the six degenerate states of cerium are split into a doublet and a quartet (of which the doublet is lower) with an energy separation Δ. The energy eigenvalues and their eigenfunctions are given by Murao and Matsubara.[17]

A direct calculation with Eqs. (5)–(9) gives first of all the general result that the matrix elements of H_{sf} between states belonging to different multiplets do not give divergent logarithmic contribution. In other words the Kondo effect can coexist with the crystal-field splitting only when the crystal field does not completely remove the degeneracy. This result agrees with the intuitive argument that any energy gap between the localized levels prevents the internal degree of freedom of the spin from being fully effective in causing the singularity. Neglecting Γ^2 terms other than the logarithmically divergent ones, we obtain after some algebraic manipulation

$$\chi^{(0)} = (C/T) F(T), \tag{10}$$

where $C = N(g\mu_B)^2 J(J+1)/3k_B$ is the Curie constant, and $F(T)$ is a correction factor due to the crystal field:

$$F(T) = \tfrac{4}{7}(e^{\beta\Delta} + 2)^{-1}[\tfrac{1}{12}(26 + 5e^{\beta\Delta}) + \tfrac{8}{3}(\beta\Delta)^{-1}(e^{\beta\Delta} - 1)]; \tag{11}$$

and

$$\chi^{(2)} = (C/T)(2\Gamma\rho)^2 \ln(k_B T/D) \varphi(T), \tag{12}$$

with the usual significance of the symbols and with the correction factor $\varphi(T)$ given by

$$\varphi(T) = \frac{1}{189}\frac{1}{e^{\beta\Delta}+2} \times\left[986+125\,e^{\beta\Delta}+960\,\frac{e^{\beta\Delta}}{e^{\beta\Delta}+2}+\frac{1}{\beta\Delta}(e^{\beta\Delta}-1)\left(1216+960\frac{e^{\beta\Delta}-2}{e^{\beta\Delta}+2}-480\frac{e^{\beta\Delta}+1}{e^{\beta\Delta}-1}+\frac{960}{\beta\Delta}\right)\right]. \quad (13)$$

Other nondivergent terms in $\ln(k_B T+\Delta)$ would be of some relevance only at high temperatures (in the limit $\beta\Delta \to 0$).[22] However, in this limit the whole $\chi^{(2)}$ contribution is very small and can be completely neglected with respect to $\chi^{(0)}$. In the opposite limit ($\beta\Delta \to \infty$), Eq. (13) correctly gives only the contribution due to the ground doublet states.

By comparing the predictions of our theory with the available experimental data,[6,7] we may determine for La:Ce the values of the important parameters Δ and T_K (T_K is defined as the temperature where perturbation theory breaks down). The results are obviously dependent on the value of D and the expression of T_K. In particular, the crystal field will affect T_K in such a way that the usual formula $T_K = De^{-1/2|\Gamma|\rho}/k_B$ has to be revised. In order to determine T_K we have evaluated, in the framework of the $\vec{J}\cdot\vec{s}$ model, the resistivity of the La:Ce alloy, taking into account the influence of the crystal field on the Kondo system.[15]

Because of the influence of the crystal field we obtain a Kondo effect in La:Ce for $\Gamma > 0$. As the complete calculation will be reported elsewhere, here we shall only give the equation which allows us to evaluate T_K in the low-temperature range. We have

$$\Psi(T_K) = (2\Gamma\rho)^{-1}, \quad (14)$$

where

$$\Psi(T) = [15+192(1+e^{\beta\Delta})^{-1}+78e^{-\beta\Delta}]^{-1} \times\{[-25+96(1+e^{\beta\Delta})^{-1}+70e^{-\beta\Delta}]\ln k_B T/D+[20+48(1+e^{\beta\Delta})^{-1}+4e^{-\beta\Delta}]\ln(|k_B{}^2T^2-\Delta^2|/D^2)\}. \quad (15)$$

Taking $D = 700$ K (which is of the order of magnitude suggested by Cornut and Coqblin[14]), we obtain the best fit for $T_K = 0.1$ K and $\Delta = 60$ K.

To allow a complete comparison with the experimental data,[6,7] the theoretical curves of the magnetic susceptibility and its reciprocal are shown in Figs. 1 and 2, respectively, together with the experimental data. As can be easily seen, the agreement between theory and experiment is very good on the whole range of temperatures. On the other hand, our estimate of T_K is in good agreement with the values found by Flouquet[5] ($T_K = 100$ mK) and by other authors.[1-4] As far as the sensitivity of the fit to the value of T_K is concerned, we should note that if one varies

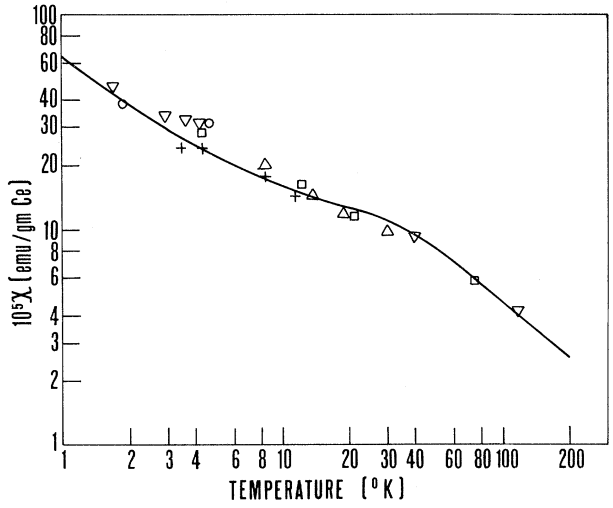

FIG. 1. Susceptibility versus temperature for the La:Ce system. The experimental points are taken from Ref. 6. The continuous curve gives the predictions of the theory.

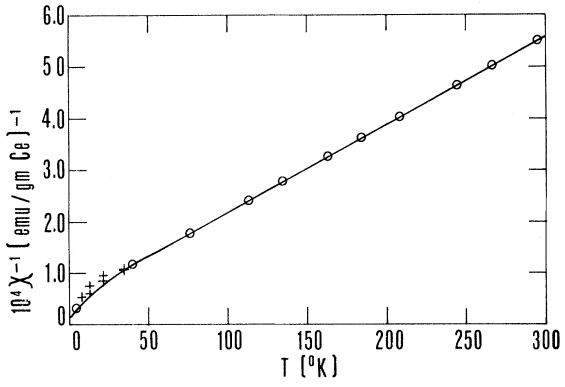

FIG. 2. Reciprocal susceptibility versus temperature for La:Ce system. The experimental points are taken from Ref. 7. The continuous curve gives the predictions of the theory.

T_K in the range 0.05–0.2 K, it is possible to obtain again a good agreement with the experimental data by a slight adjustment of Δ. On the other hand for $T_K > 1$ K we obtain a poor agreement with the experimental points, particularly in the low-temperature region, even if we allow a Δ variation in the range 30–300 K.

Our calculations unquestionably show the importance of the crystal-field splitting for the magnetic susceptibility of Kondo systems and suggest that crystal fields should play a prominent role also for other properties of the Kondo systems. This possibility, as well the extension of the theory to other crystal-field symmetries, is at present under examination.

†Work supported in part by the National Research Council.

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High- and Low-Field Limits for the Hall Coefficient of Potassium

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The Hall coefficient (R) for *homogeneous* potassium single crystals was measured at 4.2°K in magnetic fields (H) up to 85 kG. Above 15 kG, R approached H-independent values in excellent agreement with free-electron calculations. Thus, the Fermi surface must be simply connected. Below 15 kG, R exhibited weak H dependence stemming almost unambiguously from scattering anisotropy (due predominantly to phonons). At low H, R is compared with pseudopotential calculations. Correlations between R and magnetoresistance are identified for either scattering or inhomogeneity phenomena.

A recent commentary[1] concerning the anomalous linear magnetoresistance (MR) of potassium (K) concluded with the challenge "... because so long as there are doubts about the behavior of potassium, there must be doubts about our fundamental understanding of metals." Analogously, the anomalous decrease of the Hall coefficient (R) at high magnetic fields (H) presents an equivalent challenge. Traditional microscopic theories[2] for *homogeneous*[3] conductors with simply connected Fermi surfaces (FS) rigorously predict that R must approach an H-independent value ($R_\infty = -1/ne$; n = electron density) in the high-field limit where $\omega_c\tau \gg 1$, ω_c being the cyclotron frequency and τ the relaxation time. Thus for K, In, and Al, whose FS are generally believed