ESR study of the spin fluctuation dynamics of a cerium Kondo impurity in $La_{1-x}Ce_xInCu_2$

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ESR of gadolinium localized moments introduced as a probe into $La_{1-x}Ce_xInCu_2$ ($0 \leqslant x \leqslant 0.2$) is studied in the temperature range 1.6–60 K. Static magnetic susceptibility measurements are performed. The dependence of the Ce-ion spin-fluctuation rate on temperature and concentration x is found and the exchange coupling parameters are determined as well.

An important source of information on the properties of f centers in Kondo compounds is the temperature dependence of the rate of the spin fluctuations of these centers. This characteristic can be studied by ESR measurements. Kondo fluctuations rule out direct observation of an ESR signal from the spins of Kondo centers, because the resonance line is wide. A small amount of dopant with a well-localized magnetic moment (gadolinium or manganese) is therefore usually introduced to serve as a spin probe. The indirect exchange interaction of the probe spin with the spins of the Kondo ions gives rise to exchange fields, as can be seen directly from the magnetic-resonance line. In particular, temporal fluctuations caused in the exchange fields by the spin fluctuations of Kondo centers constitute a source of broadening of the resonance line of the probe. The magnitude of this component of the linewidth is determined by the rate of spin fluctuations of the Kondo ion. This method has been used to study several compounds: $Y_{1-x-y}Ce_xGd_yAl_2$ (Ref. 1), $Ce_{1-y}Gd_yCu_2Si_2$, and $Ce_{1-y}Gd_yAl_3$ (Ref. 2). Our purpose in the present study was to use the ESR method with a Gd^{3+} spin probe to learn about the dynamics of the spin fluctuations of the cerium ion in the alloy $La_{1-x}Ce_xInCu_2$. The fairly high Kondo temperature ($T_K \approx 5$ K) makes it possible to observe ESR signals at temperatures both above and below T_K. This compound has a cubic crystal structure and a long-range antiferromagnetic order, which arises at high cerium concentrations below a temperature of 2 K (Ref. 3).

We have also made an attempt to determine the constant of the Ruderman–Kittel–Kasuya–Yosida (RKKY) indirect exchange interaction between cerium ions from the ESR data. The ratio of the magnitude of this exchange interaction to the Kondo energy is an important parameter, determining the nature of the ground state of the Kondo lattice.

1. EXPERIMENTAL PROCEDURE

Polycrystalline samples of $La_{1-x-y}Ce_xGd_yInCu_2$ ($x = 0, 0.01, 0.1, 0.15, 0.2$; $y = 0, 0.1$) were prepared in an induction furnace in an atmosphere of pure helium. The starting components had a purity of 99.90% by weight. The crucible material was molybdenum. X-ray diffraction analysis revealed that all the samples consisted of a single phase and had a Heusler cubic structure[4] with a lattice constant of 6.8 Å. The cerium atoms form an fcc lattice.

The gadolinium concentration must be low enough that we can avoid any significant broadening of the ESR line of Gd^{3+} due to the dipole-dipole interaction between gadolinium ions and also possible magnetic order of these ions at low temperatures. At a cerium concentration above $x \approx 0.3$, the ESR signal is not observed at the gadolinium concentration selected.

a) The ESR measurements were carried out with a B-ER 418S rf spectrometer at a frequency of 9400 MHz over the temperature range from 1.6 to 60 K. The gadolinium-doped samples exhibited a single ESR line. This line had the asymmetric shape characteristic of bulk metals and consisted of a mixture of equal parts of Lorentzian dispersion and absorption curves (χ' and χ''). The signal-to-noise ratio was at least 100.

Figure 1 shows the temperature dependence of the width ΔH of the ESR line of gadolinium in the compound $La_{1-x-y}Ce_xGd_yInCu_2$ with $y = 0.01$. At $x = 0$ we find the linear dependence characteristic of normal metals. When cerium ions are added to the $LaInCu_2$, the width of the ESR line of Gd^{3+} increases. The dependence $\Delta H(T)$ becomes nonlinear. With increasing cerium concentration, the initial slope $\partial(\Delta H)/\partial T$ of this curve increases continuously.

Figure 2 shows the temperature dependence of the g-factor. The error in the determination of the position of the resonance line is due to the width of this line. The large widths observed for the resonance line, which increase upon the addition of cerium, accordingly lead to large errors in the determination of the g-factor. Nevertheless, it can be concluded from the experimental data in Fig. 2 that $x = 0$ the value of the g-factor is constant over the temperature range studied, at a value of 2.010 ± 0.015. With increasing cerium content, we see a tendency for the g-factor to decrease and for a temperature dependence to arise.

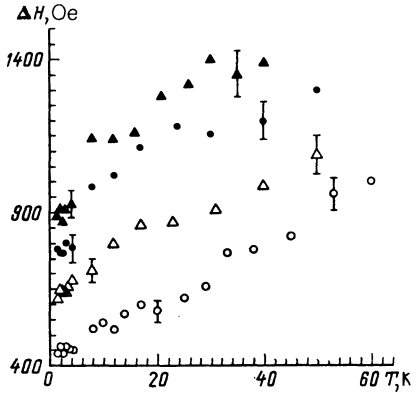

FIG. 1. Temperature dependence of the width of the Gd^{3+} ESR line in the compound $La_{1-x}Ce_xInCu_2$. ○—$x = 0$; △—0.1; ●—0.15; ▲—0.2.

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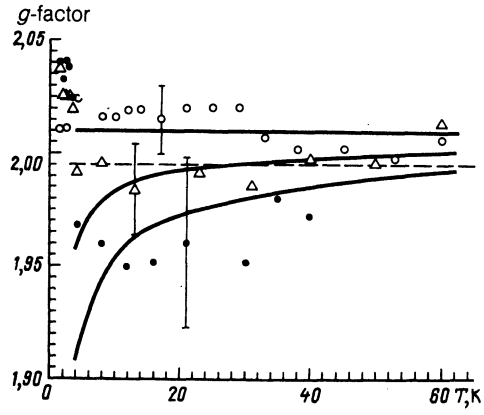

FIG. 2. Temperature dependence of the Gd^{3+} ESR g-factor in the compound $La_{1-x}Ce_xInCu_2$. ○—$x=0$; △—0.1; ●—0.2.

At low temperatures ($T<4$ K) the g-factor increases substantially as $T\to 0$. This behavior stems from the low-temperature ordering of the spins of the gadolinium ions. In interpreting our experimental results below, we will discuss only the temperature region ($T>4$ K) in which the influence of ordering effects on the Gd^{3+} ESR is negligible in comparison with other mechanisms which we will be discussing here.

b) The static magnetic susceptibility of $La_{1-x}Ce_xInCu_2$ was measured by the Faraday method in a field $H\sim 1$ kOe. Figure 3 shows the temperature dependence of the reciprocal magnetic susceptibility χ_{Ce}^{-1}, where χ_{Ce} is the difference between the magnetic susceptibilities of the compound $La_{1-x}Ce_xInCu_2$ (χ_{La-Ce}) and of the $LaInCu_2$ matrix (χ_{La}). The weak concentration dependence of the susceptibility, $\chi_{Ce}(x)$, implies that spin-spin directions between cerium ions are negligible at $X\lesssim 0.2$. The nonlinearity in $\chi_{Ce}^{-1}(T)$ in the temperature interval 10 K $<T<$ 50 K is due to Stark splitting of the $J=5/2$ state of the cerium ion in the cubic crystal field, into a quartet Γ_8 and a doublet Γ_7, with an energy gap $\Delta\approx 90$ K, according to Ref. 5. It is also due to Kondo screening of the cerium spins. At low temperatures ($T\ll\Delta$), at which the susceptibility χ_{Ce} is determined by the twofold-degenerate Kramers level Γ_7, its temperature dependence can be described approximately by the Curie–Weiss curve with a constant $\theta\approx -3$ K. This value is close to the value found for θ in Ref. 5.

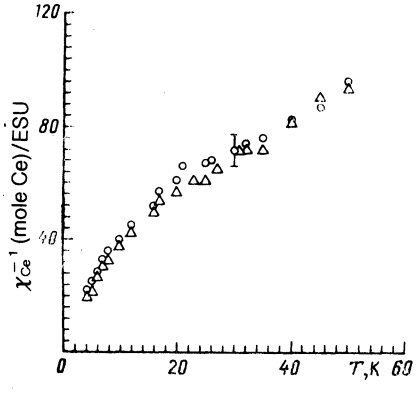

FIG. 3. Temperature dependence of the reciprocal magnetic susceptibility χ_{Ce}^{-1} of the compound $La_{1-x}Ce_xInCu_2$. △—$x=0.1$; ○—0.2.

2. DISCUSSION OF THE ESR RESULTS

The Gd^{3+} ion has a spin $S=7/2$. The Zeeman splitting for the ion in a crystal field generally has a nonuniform spacing, because of the slight admixture of higher-lying states with a nonzero orbital angular momentum in the wave function of the ground state. This nonuniform spacing might lead to local lines corresponding to transitions between different spin projections (the "fine structure" of the ESR line), but the exchange interactions between the spins of the gadolinium mix these transitions, giving rise to a single line of Lorentzian shape. The crystal-field effects contribute only a constant increment in the width of the ESR line.

When a sample has no Kondo impurity, the temperature dependence of the width of the ESR line (Fig. 1) is determined by the standard expression for normal metals:

$$\Delta H=a+bT. \tag{1}$$

The constant contribution $a\approx 405$ Oe is determined by an exchange interaction modulated by effects of the fine structure and of the dipole-dipole interaction between gadolinium ions. The expression for the slope b of the temperature dependence depends on how close the system is to the electron bottleneck.[6] This regime prevails if the spin-lattice relaxation of the conduction electrons is weak in comparison with the inverse scattering of electrons by gadolinium spins. Korringa relaxation is not seen in its totality, and the constant b becomes dependent on the spin-lattice relaxation of the conduction electrons. We have established that the addition of a small amount of cerium ($x=0.01$) to a sample causes a substantial increase in the rate of the spin-lattice relaxation of the conduction electrons but does not cause any significant increase in the high-temperature slope $\partial(\Delta H)/\partial T$. It can thus be concluded that the $La_{1-y}Gd_yInCu_2$ ($y=0.01$) system is far from the electron bottleneck and that the temperature dependence of the linewidth is governed by the Korringa relaxation of gadolinium spins in its "pure" form. If the Hamiltonian of the s-f exchange interaction of the spin of a conduction electron, s_e, with the spin of an impurity, S, is written in the form

$$H^{sf}=-J_{Gd}{}^{sf}\mathbf{S}_{Gd}\mathbf{s}_e, \tag{2}$$

the constant b is given by

$$b=\pi k_B(J_{Gd}{}^{sf}N(\varepsilon_F))^2/g_{Gd}\mu_B. \tag{3}$$

Here J^{sf} is the exchange integral of the interaction of the spin of a conduction electron with an impurity spin, and $N(\varepsilon_F)$ is the density of states of the conduction electrons per atom, per spin direction. From the experimental value $b=10\pm 2$ Oe/K we find the value $|J_{Gd}^{sf}N(\varepsilon_F)|=0.020\pm 0.004$. The sign of the exchange integral can be determined from the electron Knight shift:

$$\Delta g_N=J_{Gd}{}^{sf}N(\varepsilon_F). \tag{4}$$

Because of the large experimental error, it is not possible to determine the g-factor for the ESR of gadolinium accurately. In any case, the shift of the g-factor with respect to the value $g_0=1.995$, characteristic of the free gadolinium ion, is positive: $\Delta g_{exp}=0.015\pm 0.015$. It follows that the exchange integral for gadolinium is of a ferromagnetic nature: $J_{Gd}^{sf}>0$. Estimating the density of states of the conduction band in the free-electron model, $N(\varepsilon_F)\approx 0.2$

(eV·spin·atom)$^{-1}$, we find $J_{Gd}^{sf} \approx 0.1$ eV.

When cerium ions are incorporated in the system, the primary cause of the broadening of the ESR line of gadolinium is the indirect exchange interaction between cerium and gadolinium ions through conduction electrons:

$$H_{Ce-Gd}^{ex} = -\sum_{ij} J_{ij}^{ex} S_{Gd}^{i} S_{Ce}^{j}. \quad (5)$$

In the RKKY model the exchange integral is

$$J_{ij}^{ex} = J_0 v_0 \cos(2k_F r_{ij})/r_{ij}^3, \quad (6)$$

where v_0 is the volume per lattice site, k_F is the Fermi momentum, and we are using the constant

$$J_0 = J_{Ce}^{sf} J_{Gd}^{sf} N(\varepsilon_F)/8\pi. \quad (7)$$

Interaction (5) is manifested as two contributions to the ESR linewidth of the gadolinium ion. One involves the appearance of a nonzero polarization $\langle S_{Ce}^z \rangle$ of the cerium spins in an external field. This polarization is proportional to the susceptibility of cerium and leads to a static exchange field at gadolinium ion i. The magnitude of this field is

$$H^i = -\langle S_{Ce}^z \rangle \sum_j J_{ij}^{ex}/2\mu_B. \quad (8)$$

The summation over j in (8) is carried out over the sites occupied by cerium ions. Since the cerium ions are distributed randomly through the crystal, and the potential in (6) oscillates rapidly over distance, the shift of the resonance frequency associated with (8) has a spatial dispersion. This dispersion causes inhomogeneous broadening of the ESR line of the Gd^{3+} ions. This contribution to the linewidth was calculated in Ref. 7:

$$\Delta H_1 = \frac{2\pi}{54} x |J_0| \omega_0 \chi_{Ce}/\mu_B^2. \quad (9)$$

The quantity $\Delta H_1(T)$ has a temperature dependence like $\chi_{Ce}(T)$. On the other hand, if we take the spatial average of exchange fields (8), we can find the shift of the g-factor with respect to its value at $x = 0$ (Ref. 1):

$$\Delta g = (g_{Ce} - 1) x \chi_{Ce} \sum_j J_{ij}^{ex}/g_{Ce}\mu_B^2. \quad (10)$$

The shift Δg is also proportional to the static susceptibility χ_{Ce}.

Another contribution of the interaction (5) to the width of the ESR line of gadolinium stems from the relaxation of the Gd^{3+} spin to spin fluctuations of the cerium ion. According to Ref. 1, this contribution is

$$\Delta H_2 = xAT\chi_{Ce}(\Gamma_7)\tau, \quad (11)$$

where

$$A = 2k_B(g_{Ce} - 1)^2 \sum_j (J_{ij}^{ex})^2/g_{Gd} g_{Ce}^2 \mu_B^3 \hbar,$$

and $\chi_{Ce}(\Gamma_7)$ is the static magnetic susceptibility of the Γ_7 ground state of the cerium ion. The quantity τ in (11) is the time scale of the spin fluctuations of the cerium Kondo impurity. The temperature dependence of the contribution ΔH_2 is determined by the temperature dependence $\chi_{Ce}(\Gamma_7)$ and the temperature dependence of the parameter in which we are interested, $\tau(T)$.

The analysis of experimental data in Refs. 1 and 2 ignored the contribution of (9) to the linewidth, stemming from the static spread of exchange fields. That simplification is legitimate at high temperatures, but at low temperatures this contribution outweighs the ΔH_2 contribution, which tends toward zero in the Fermi-liquid regime at $T < T_K$.

In general, there would be yet another contribution to the Gd^{3+} ESR linewidth. That is the contribution from the spatial dispersion of the fine-structure constants of the gadolinium ions, which itself stems from local lattice deformations which arise when lanthanum ions are replaced by cerium ions. This contribution is evidently independent of the temperature and is proportional to the cerium concentration x. Since the difference between the lattice constants of $LaInCu_2$ and $CeInCu_2$ is no greater than[4] 1%, we can assume that the local lattice deformations resulting from the replacement of lanthanum ions by cerium ions are insignificant. On this basis, we also ignore that contribution.

The final expression for the width of the Gd^{3+} ESR line as a function of the temperature and the cerium concentration is thus

$$\Delta H(x, T) = a + bT + \Delta H_1(x, T) + \Delta H_2(x, T), \quad (12)$$

where b, ΔH_1, and ΔH_2 are given by (3), (9), and (11), respectively. This equation can be used to estimate the spin-fluctuation time τ of the cerium ion.

The static magnetic susceptibility of the Γ_7 ground state of cerium, which appears in (12), is given by

$$\chi_{Ce}(\Gamma_7) = C/(T - \theta). \quad (13)$$

At temperatures ($T \lesssim 10$ K) much lower than the size of the energy gap between the Γ_7 and Γ_8 states, $\Delta \approx 90$ K (Ref. 5), the susceptibility of the cerium ion is determined by a Kramers doublet. At these temperatures we thus have $\chi_{Ce} \approx \chi_{Ce}(\Gamma_7)$. Comparing Eq. (13) with the measured susceptibility χ_{Ce}^{-1} under this assumption (Fig. 3), we find that over the cerium concentration range studied we have $C = 0.31 \pm 0.03$ esu·K/(mole Ce) and $\theta = -(3 \pm 1)$ K.

The parameters $|J_0|$ and $\Sigma_j (J_{ij}^{ex})^2$ in (12) are unknown. Since the contributions bT and $\Delta H_2(x, T)$ tend toward zero in the limit $T \to 0$, the residual value of the contribution $\Delta H_1(x, T)$ is, according to (12),

$$\Delta H_1(x, 0) = \Delta H(x, 0) - a. \quad (14)$$

This quantity can be determined from the ESR results at low temperatures, by carrying out a linear extrapolation of the functional dependence $\Delta H(x, T)$ to absolute zero. The experimental values found for this contribution in this manner for various cerium concentrations conform to an expression $\Delta H_1(x, 0) = 1950\ x$ Oe. Comparing this expression with (9), we find

$$|J_0| \approx 17{,}0 \text{ K}. \quad (15)$$

From (6), estimating k_F in the free-electron approximation, and evaluating the corresponding lattice sums, we then find

$$\left| \sum_j J_{ij}^{ex} \right| = |J_0| \left| \sum_j v_0 \cos(2k_F r_{ij})/r_{ij}^3 \right| \approx 25{,}2 \text{ K}, \quad (16)$$

$$\sum_j (J_{ij}^{ex})^2 = J_0^2 \sum_j v_0^2 \cos^2(2k_F r_{ij})/r_{ij}^6 \approx 66{,}2\ \text{K}^2. \quad (17)$$

Since the experimental values of the shift $\Delta g(x, T)$, of the g-factor are negative, we find from (10)

$$\sum_j J_{ij}^{ex} > 0.$$

Since

$$\sum_j \cos(2k_F r_{ij})/r_{ij}^3 < 0,$$

we find $J_0 < 0$ from (6). The interaction of the nearest cerium and gadolinium ions is thus ferromagnetic, and the exchange integral is $J_{\text{Gd-Ce}}^{ex} \approx 2.2$ K.

The curves of the temperature dependence of the g-factor found for $x = 0.1$ and 0.2 with this estimate of the lattice sum $\Sigma_j J_{ij}^{ex}$, with the help of expression (10) and the experimental susceptibilities $\chi_{\text{Ce}}(T)$, are the solid lines a and b, respectively, in Fig. 2. These curves do not contradict the corresponding experimental values of the g-factor.

Knowing the values of the pertinent constants, we can now determine the frequency of the spin fluctuations. From the experimental values of the Gd^{3+} ESR linewidth and of the susceptibility $\chi_{\text{Ce}}(T)$, we can find the effective rate τ^{-1} of the spin fluctuations of the cerium ion as a function of the temperature and the concentration, using Eqs. (9) and (11)–(13). The results are shown in Fig. 4. There is some increase in $\tau^{-1}(T)$ at high temperatures. This increase results from a Korringa relaxation of the local moment into thermal fluctuations of the spin density of conduction electrons. With decreasing temperature, $\tau^{-1}(T)$ reaches saturation, because of quantum Kondo fluctuations. It shows a tendency to increase toward absolute zero. The rate of fluctuations of the spin of the cerium ion in the compound $Y_{1-x}Ce_xAl_2$ ($x \lesssim 0.4$) exhibits a similar temperature dependence.[1] In that case, the Ce^{3+} ions are in a Kondo-impurity regime. The Kondo temperature of the cerium ions in the alloy $La_{1-x}Ce_xInCu_2$ can be estimated from the minimum value of the fluctuation rate: $T_K = \hbar/\tau k_B \approx 6$ K. This value agrees with the results of Ref. 5.

The concentration dependence $\tau^{-1}(x)$ is within the experimental error; over the concentration range studied, $0 < x \leqslant 0.2$, the dynamics of the spin fluctuations apparently develops in the impurity regime.

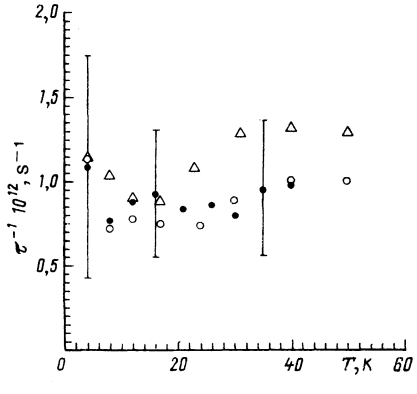

FIG. 4. Temperature dependence of the rate of spin fluctuations of the cerium ion in the compound $La_{1-x}Ce_xInCu_2$. Δ—$x = 0.1$; ○—0.15; ●—0.2.

It is interesting to note the sign and magnitude of the exchange integral for the exchange of the cerium spin with conduction electrons, J_{Ce}^{sf}. This integral can be found from (7) with the help of the values found for J_0 and $J_{\text{Gd}}^{sf} N(\varepsilon_F)$. The result is $J_{\text{Ce}}^{sf} \approx -1.8$ eV. The exchange integral J^{sf} in a metal is known to be determined by two competing contributions:

$$J^{sf} = J^{sf}(at) + J^{sf}(cov).$$

Here $J^{sf}(at) > 0$ is the constant of the direct exchange interaction. The second term, $J^{sf}(cov) < 0$, is determined by s-f hybridization processes. The signs we found experimentally for J^{sf} agree with that for the spin of the cerium ion, in contrast with gadolinium, for which the second, covalent, mechanism dominates and leads to antiferromagnetic coupling with conduction electrons and to the Kondo effect.

The rapid increase in the width of the resonance line with increasing cerium concentration and the effects of the magnetic ordering of the gadolinium impurity itself at low temperatures rule out a direct study of the effects of exchange interactions between cerium ions. These interactions give rise to a correlation between the Kondo centers and to an antiferromagnetism with a small magnetic moment of the sublattices.[3] Nevertheless, definite information about the magnitude and sign of the exchange interaction between cerium ions can be extracted from our results. For example, the exchange constant $\tilde{J}_{\Gamma_7}$ of the interaction between the effective spins $\tilde{S} = 1/2$ of the Kramers doublet,

$$H_{ex}^{\text{Ce-Ce}} = -\tilde{J}_{\Gamma_7} \tilde{\mathbf{S}}_i \tilde{\mathbf{S}}_j \quad (18)$$

is

$$\tilde{J}_{\Gamma_7}^{\text{Ce-Ce}} = J_{\text{Gd-Ce}}^{ex} (J_{\text{Ce}}^{sf}/J_{\text{Gd}}^{sf}) ((g_{\text{Ce}} - 1)\tilde{g}_{\Gamma_7}/g_{\text{Ce}})^2, \quad (19)$$

where $\tilde{g}_{\Gamma_7} = -1.43$ is the effective g-factor of the Γ_7 doublet. Using the values found above for the constants, $J_{\text{Gd-Ce}}^{ex} \approx 2.2$ K, $J_{\text{Ce}}^{sf} \approx -1.8$ eV, and $J_{\text{Gd}}^{sf} \approx 0.1$ eV, we find $\tilde{J}_{\Gamma_7} \approx -2.2$ K for the nearest cerium spins. The sign of the constant corresponds to an antiferromagnetic coupling, and the scale of the exchange field in the regular $CeInCu_2$ system, $\omega_{\text{RKKY}} \sim z|\tilde{J}_{\Gamma_7}|\tilde{S}(\tilde{S}+1)/3 \approx 7$ K, where z is the coordination number of the cerium sublattice, is comparable to the energy of Kondo fluctuations. This result suggests that an antiferromagnetic RKKY field on the order of the Kondo energy does not prevent—and in fact takes active part in—the formation of a heavy-fermion band. As a result, the tunneling of Kondo singlets through the lattice becomes coherent. The importance of the RKKY interaction in describing the low-temperature dynamics of Kondo lattices has been discussed in some recent theoretical papers (e.g., Ref. 8).

In summary, a study has been made of the temperature dependence and the concentration dependence of the rate of the spin fluctuations of the cerium ion in the compound $La_{1-x}Ce_xInCu_2$. The constants of the exchange interaction of cerium spins with conduction electrons and with each other have been determined. Our results indicate that the cerium ions are in a Kondo impurity regime at concentrations $x \lesssim 0.2$.

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