Kleber (McMillan, New York, 1961), p. 135.

[11] R. L. Cohen, M. Eibschütz, and K. W. West, Phys. Rev. Lett. 24, 383 (1970), and J. Appl. Phys. 41, 898 (1970).

[12] E. E. Vainshtein, S. M. Blokhin, and Yu. B. Paderno, Fiz. Tverd. Tela 6, 2909 (1964) [Sov. Phys. Solid State 6, 2318 (1965)].

[13] J. C. Nickerson, R. M. White, K. N. Lee, R. Bachmann, T. H. Geballe, and G. W. Hull, Jr., Phys. Rev. B 3, 2030 (1971).

[14] L. L. Hirst, Phys. Kondens. Mater. 11, 255 (1970).

[15] J. G. Huber and M. B. Maple, J. Low Temp. Phys. 3, 537 (1970).

[16] B. Coqblin and A. Blandin, Advan. Phys. 17, 281 (1968); B. Coqblin, J. Phys. (Paris) Suppl. 32, C1-599 (1971).

[17] Z. Fisk, B. T. Matthias, and E. Corenzwit, Proc. Nat. Acad. Sci. 64, 1151 (1969).

Nuclear-Orientation Studies of *La*Ce, *Au*Ce, and *Ag*Ce

J. Flouquet
Laboratoire de Physique des Solides associé au Centre National de la Recherche Scientifique, 91 Orsay, France

(Received 11 May 1971)

LaCe^{137m} alloys prepared by proton bombardment of La metal have been studied by orientation of the Ce^{137m} nuclei. From the variation of the anisotropy of the emitted γ rays with applied field, the Kondo temperature is estimated to be 0.1 K. *Au*Ce and *Ag*Ce have also been studied using the same technique. The results for the three systems are compared with those obtained by other methods.

For a rare-earth impurity in a metallic lattice, the coupling between the local spin J and the conduction electron s can be described by the Hamiltonian $H=\Gamma_{\mathrm{eff}}\vec{J}\cdot\vec{s}$. There are two contributions to Γ_{eff}: a positive exchange term and an antiferromagnetic coupling due to the mixing between conduction and local electrons.[1] The existence of a resistance minimum for *La*Ce shows that apparently $\Gamma_{\mathrm{eff}}<0$, while for *Mg*Ce,[2] with no resistance minimum, apparently $\Gamma_{\mathrm{eff}}>0$. From resistivity measurements on *La*Ce, Kim and Maple,[3] Gey and Umlauf,[4] Sugawara and Eguchi,[5] and Wollan and Finnemore[6] find a Kondo temperature T_{K} less than 1 K, while Edelstein *et al.*[7] from susceptibility measurements estimate T_{K} to be about 20 K. Recently, Grobman[8] found an anomaly in the thermoelectric power near 20 K which had not been observed by Sugawara and Eguchi.[5] We present nuclear orientation measurements on *La*Ce alloys and compare them with the results obtained on *Au*Ce[9] and *Ag*Ce.

The *La*Ce alloy is obtained directly by proton bombardment of a La metal foil (99.9+% pure La provided by Koch Light). The 35-MeV incident protons form Ce^{137m} *in situ* by the $(p, 3n)$ reaction on La; 48 hours after irradiation the only activities visible were those of the 39-h half-life Ce^{137m} and Ce^{139}. The beam heating during bombardment may well affect the metallurgical state of the sample. The foil was point soldered onto a copper wire for thermal contact, and then cooled in an adiabatic demagnetization cryostat to temperatures between 12 and 30 mK. The anisotropy of the 255-keV γ rays from the radioactive nuclei was then measured as a function of applied field and temperature with fields from 1.5 to 25 kOe. Since La is a superconductor, possible reduction of flux penetration is an experimental problem. Sugawara and Eguchi[10] find a critical field $H_{c1}(0°\mathrm{K})$ of 400 Oe for the hexagonal α phase, but Mamiya, Fukuroi, and Tanama[11] find 1600 Oe for the cubic β phase. So since these values depend strongly on the sample purity, it is quite possible that flux penetration was reduced at the lowest fields (1500 Oe) for any parts of the sample in the β phase. This could lead to an overestimation of T_{K} in what follows. This estimation is also complicated by the presence of the two phases: In a site with hexagonal symmetry, a Ce ion is characterized by a highly anisotropic g factor and hyperfine coupling constant A, while in cubic symmetry, as long as the crystal-field splitting Δ is much greater than $g\mu_{\mathrm{B}}H$, the ion has an isotropic g factor and hyperfine coupling constant. To simplify matters, we will assume in the analysis that the sample was entirely in the cubic β phase.

In a nuclear orientation experiment, the measured γ anisotropy can be directly related to the population of the nuclear sublevels of the parent[12] (in this case Ce^{137m}). When the nucleus is contained in a dilute paramagnetic impurity the difficulty is that there is in general no simple relation between the anisotropy and the magnetization M of the impurity[13]: The concept of a hyperfine field H_n is valid only if the ionic relaxation τ_e or the precession is rapid with respect to a nuclear Larmor period T_n. However, the saturation value of the anisotropy in a high magnetic field gives the hyperfine coupling constant A and the saturation hyperfine field $H_{\rm sat}$ through the relation

$$H_{\rm sat}=AJ/g_N\mu_N,$$

where J is the ionic spin and g_N the nuclear g factor. As a first approximation, $H_{\rm sat}$ for a given ion is proportional to the localized moment. For 3*d* magnetic impurities, $H_{\rm sat}$ depends strongly on the host metal ($H_{\rm sat}=400$ kOe for *Au*Mn and 278 kOe for *Cu*Mn[14]) and it is very different from the value H_0 in a nonmetal (about 750 kOe for Mn^{2+}). The coupling with the conduction electrons is strong, giving large phase shifts at the Fermi level (*d*-level broadening $\Delta\sim 1$ eV). For rare-earth impurities, $\Delta\sim 0.02$ eV, normally $\Delta\ll E_0$ (where E_0 is the energy difference between the f level and the Fermi energy), and saturation fields vary little with the host[15] and are close to the value H_0 in nonmetals. $H_{\rm sat}$ at low temperatures is then characteristic of the ionic ground state determined by the crystal field. However, the coupling with the conduction electrons leads to a positive deviation of $H_{\rm sat}/\mu_{\rm sat}$ from the ionic value[14, 15]; this deviation is important when E_0 becomes the same magnitude as Δ.

The behavior as a function of magnetic field can be used to study the $\vec{J}\cdot\vec{s}$ coupling. We will consider only the zero-coupling and strong-coupling limits. (a) For zero coupling, the anisotropy can be calculated from the Hamiltonian

$$\mathcal{H}=A\vec{I}\cdot\vec{J}+g_J\mu_B\vec{H}\cdot\vec{J}+g_I\mu_N\vec{H}\cdot\vec{I},$$

where $\vec{I}$ is the nuclear spin. This corresponds to $\tau_e\gg T_n$ and is also called the free-spin or slow-relaxation limit.[13] (b) In the limit of strong coupling (i.e., fast ionic relaxation $T_K\gtrsim 0.1$ K), the hyperfine-field concept H_n is valid for all values of applied field H; except for the $H_{\rm sat}/\mu_{\rm sat}$ deviation, the γ anisotropy measurement can then be interpreted as a magnetization measurement. The fact that a system is observed to fit case (a) is proof only that $\Gamma_{\rm eff}$ is small, but $\Gamma_{\rm eff}$ can nevertheless be negative (e.g., *Au*Mn[13]). For cases intermediate between the limits (a) and (b) it appears that a fit of the nuclear orientation to the strong-coupling limit produces (Fig. 2) a tendency to overestimate T_K.

As we stated above, we assume the Ce to be in the cubic β-phase La. Figure 1 shows the measured γ anisotropy at different temperatures for a constant applied field. For a field of 25 kOe (Figs. 1 and 2) the γ anisotropy is approaching saturation so a T_K of 20 K is ruled out. From the saturation value of the anisotropy, we can determine a hyperfine constant $A=0.0053$ K, i.e., $H_{\rm sat}=580\pm 30$ kOe (using $g_N\mu_N I=0.69\mu_N$).[16] Coqblin, Maple, and Toulouse[17] have used the variation of the superconductivity critical temperature T_c with Ce concentration to estimate $E=-0.043$ eV, which corresponds to an occupation difference between the $|+\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ states of $n_{1/2}-n_{-1/2}=0.81$. If we assume the Ce ion to be in the Γ_7 state ($S=\frac{1}{2}$, $g=1.43\mu_{\rm sat}=0.71\mu_B$) and use $\langle r^{-3}\rangle=4.44$ a.u.[16] for an ionic Ce impurity, the hyperfine field would be[13] $H^0=630$ kOe. Using the difference in occupation of 0.81, we can estimate $H_{\rm sat}=510$ kOe. Allowing for the effect of $\Gamma\vec{J}\cdot\vec{s}$, which tends to increase the hyperfine coupling, the measured

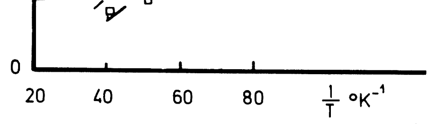

FIG. 1. Gamma-ray anisotropy of oriented ^{137m}Ce in La as a function of the reciprocal temperature for various fields.

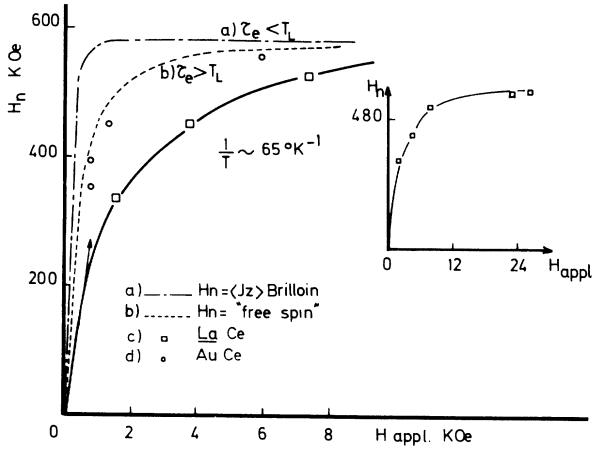

FIG. 2. H_n as a function of applied field at $T^{-1}=65$ K^{-1} for ^{137m}Ce in La (curve c) and Au, compared with the free-spin model H_n (b) and to the Brillouin function (a).

value is compatible with the assumption of a Γ_7 state for Ce.

Fig 2 assumes that a hyperfine field exists for *La*Ce. Curve (a) represents a H_n Brillouin curve for a Γ_7 state; curve (b), the equivalent hyperfine field H_n in a free-spin model with $A = 0.0035$ K; curve (c) gives the experimental data. From this curve we can estimate $T_{\rm K}$ using the relation

$$\frac{H_n}{H_{\rm sat}} = \frac{M}{M_{\rm sat}} = \frac{\mu_{\rm eff}^2}{3\mu_{\rm sat}} \frac{1}{k_{\rm B}(T+T_{\rm K})} H$$

(for low applied fields H). This gives a Kondo temperature $T_{\rm K}$ of about 100 mK. Despite the fact that the value obtained depends strongly on the assumption of β-La host, it is in total disagreement with a value of 20 K and in good agreement with the values of 150 and 200 mK found by Gey and Umlauf[4] for α-La and β-La, respectively. Edelstein *et al.*[7] analyze their results using a saturation moment for Ce of $2.5\mu_{\rm B}$, close to the high-temperature value for the Ce ion; they completely neglect crystal-field effects which are important for a rare-earth impurity (see EPR measurements of Tao *et al.*[15] and susceptibility measurements of Yoshida and Sugawara[19] on *Y*Ce). The present measurements on *La*Ce are consistent with a Γ_7 ground state; crystal-field effects are certainly important and temperature dependencies found by Edelstein *et al.*[7] cannot correspond to a "simple" Kondo system. The *Au*Ce and *Ag*Ce samples were prepared by implanting $\rm Ce^{137\mathit{m}}$ activity in a host-metal target at an energy of 100 keV. This method overcomes solubility problems, at the expense of a rather high local impurity concentration (a few hundred ppm within the penetration depth, 200 Å) and the introduction of defects into the host lattice. The measured saturation fields $H_{\rm sat}$ are 560 ± 40 kOe for *Au*Ce and 540 ± 40 kOe for *Ag*Ce. These values are compatible with a Γ_7 ground state. The experimental behavior as a function of applied field is in both cases close to that expected on a zero-coupling model. Without resistivity measurements, it is difficult to say what is the sign of $\Gamma_{\rm eff}$. We can estimate the position of the $4f$ virtual level from the thermoelectric-power results of Gainon, Donze, and Sierro.[20] Using the fact that at low temperature, magnetic impurity contribution ΔS dominates, we arrive at the relation

$$2E_0/(E_0^2+\Delta^2) = -(\Delta S)3e/\pi^2k^2T.$$

For $E_0 \gg \Delta$, we obtain $E_0 = 2\pi^2k^2T/3e(\Delta S)$. We estimate $E_0 = -0.16$ eV for *Ag*Ce and -0.10 eV for *Au*Ce. The critical value of E_0 for passage from $\Gamma_{\rm eff} > 0$ to $\Gamma_{\rm eff} < 0$ is defined by $E_{0c} = -2\Delta/\pi\rho(\epsilon_{\rm F}) \times \Gamma_1$.[21] Taking $\Gamma_1 = 0.1$ eV, $\rho(\epsilon_{\rm F}) = 0.16$ eV^{-1} atom^{-1} spin^{-1}, and $\Delta = 0.02$ eV, we find $E_{0c} = -0.8$ eV. *Au*Ce and *Ag*Ce, apparently like *Mg*Ce, correspond to $\Gamma_{\rm eff} > 0$. The position of the virtual level is consistent with a zero-coupling model (if $\Gamma_{\rm eff}$ is negative, $T_{\rm K}$ is very low).

I wish to thank, Dr. B. Coqblin and Dr. I. A. Campbell for helpful discussions, and Mr. J. Sanchez and the Low Temperature Group of the Institut de Physique Nucleáire for aid in the cryogenics.

---

[1] B. Coqblin and J. R. Schrieffer, Phys. Rev. 185, 847 (1969).

[2] F. T. Hedgcock and B. Petrie, Can. J. Phys. 48, 1283 (1970).

[3] K. S. Kim and M. B. Maple, Phys. Rev. B 2, 4696 (1970).

[4] W. Gey and E. Umlauf, Z. Phys. 242, 241 (1971).

[5] T. Sugawara and H. Eguchi, J. Phys. Soc. Jap. 26, 1322 (1969).

[6] J. J. Wollan and D. K. Finnemore, to be published.

[7] A. S. Edelstein, L. R. Windmiller, J. B. Ketterson, G. W. Crabtree, and S. P. Bowen, Phys. Rev. Lett. 26, 516 (1971).

[8] W. D. Grobman, to be published.

[9] J. Flouquet and D. Marsh, Phys. Lett. 32A, 501 (1970).

[10] T. Sugawara and H. Eguchi, J. Phys. Soc. Jap. 23, 965 (1967).

[11] T. Mamiya, T. Fukuroi, and S. Tanuma, J. Phys. Soc. Jap. 20, 1559 (1965).

[12] D. A. Shirley, Annu. Rev. Nucl. Sci. 16, 89 (1966).

[13] J. Flouquet, Phys. Rev. Lett. 25, 288 (1970).

[14] I. A. Campbell, Solid State Commun. 9, 301 (1971).

[15] L. J. Tao, D. Davidov, R. Orbach, and E. P. Chock, Phys. Rev. B (to be published).

[16] J. Blok, D. A. Shirley, and N. J. Stone, Phys. Rev. 143, 78 (1966).

[17] B. Coqblin, M. B. Maple, and G. Toulouse, to be published.

[18] J. Kondo, J. Phys. Soc. Jap. 16, 1960 (1961).

[19] S. Yoshida and T. Sugawara, Phys. Lett. 30A, 422 (1969).

[20] D. Gainon, P. Donzé, and J. Sierro, Solid State Commun. 5, 151 (1967).

[21] B. Coqblin, J. Phys. Suppl. 32, C1-599 (1971).