Observation by Nuclear Orientation under Pressure of the Magnetic State of Cerium Impurities in Lanthanum

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We describe nuclear-orientation experiments on *La*Ce alloys under pressure and show that, in an analysis with a minimum of parameters, dilute *La*Ce can be described by an ionic model in the pressure range studied (0–10 kbar). Our results are compared to indirect magnetic data extracted from measurements of transport properties.

This Letter describes the first observation of nuclear-orientation experiments (NO) under pressure. The technique applied here to the study of *La*Ce allows local magnetization measurements under pressure: To our knowledge such measurements had not previously been performed on a dilute alloy.

Because of the well-localized character of their $4f$ electrons, rare-earth impurities usually retain their ionic properties when dissolved in metals; their magnetic behavior is thus similar to that encountered in insulators. An exception is cerium for which strong mixing occurs between the f and k conduction electrons.[1] This has been observed particularly for *La*Ce where changes in transport properties due to the modifications in the k-f mixing of the Ce impurity were extensively studied[2-5] in experiments involving the pressure dependence either of the superconducting transition temperature or of the resistivity Kondo anomaly $dR/d\ln T$. Since interpretation of such experiments is rather critically dependent on the model chosen to describe the relation between magnetism and superconductivity, it is difficult to determine which model in fact best describes the impurity. For example a combination of an ionic model with the Müller-Hartmann–Zittartz theory has been used to explain the superconductivity results,[3] as has a combination of the Anderson model with the Abrikosov-Gor'kov theory.[5]

In order to test the validity of a purely ionic picture we have addressed ourselves to the following question: Is a large change in the Kondo temperature T_K (determined at low fields H, where $H < kT_K/g\mu_B$) correlated with changes in the magnetic state of the impurities in high fields, $H \gg hT_K/g\mu_B$, when the Kondo bound state is broken? If such a correlation exists, it is clear that the k-f coupling is strong, i.e., that the phase shifts φ_F of the $4f$ virtual bound states at the Fermi level are significant, and the impurity cannot be described adequately by an ionic model.

The NO experiments performed on *La*Ce under pressures up to 10 kbar provide a direct answer to this question. As in previous work at zero applied pressure,[6] the magnetization of the Ce localized moment is deduced from the variation of the Ce hyperfine field in applied magnetic fields H up to 20 kOe. From a comparison of the results in low and high applied fields at different pressures, it is shown that, in the range of applied pressures ($0 < p \lesssim 10$ kbar), the cerium impurities are well described by an ionic picture.

Some general assumptions are needed in order to relate the NO measurements to T_K and the saturation magnetization.[7] Our assumptions are (i) that the results of NO measurements under pressure may be described by a simple hyperfine field H_{eff} proportional to the local magnetization of the impurity, with a ratio $R = H_{eff}/\mu$ defined by the $4f$ orbital contribution of the Ce^{3+} ions; (ii) that the impurity is in a well-isolated $\pm\frac{1}{2}$ crystal field state; and (iii) that the susceptibility χ is related to T_K by the usual expression,

$$\chi = \mu_{eff}^2/3k(T + T_K).$$

Since, in order to make the high- and low-field regions experimentally accessible, we chose to use the hexagonal phase of *La*Ce, which has a relatively low T_K,[4] the least accurate of the three approximations is the first, i.e., the description of the NO results in terms of an effective field H_{eff} parallel to H. The true Hamiltonian is strongly anisotropic and considerably more complex.[8] The other two assumptions, in contrast, are well justified since the temperature range of the experiments was well below that where crystal-field effects become important[6,9] and also below the Kondo temperatures of the alloys.[6]

The samples of $La^{137m}Ce$ were prepared by irradiation *in situ* using a $(p, 3n)$ reaction on a lanthanum foil (35-MeV protons). The resulting Ce concentrations were less than 1 ppm. To mini-

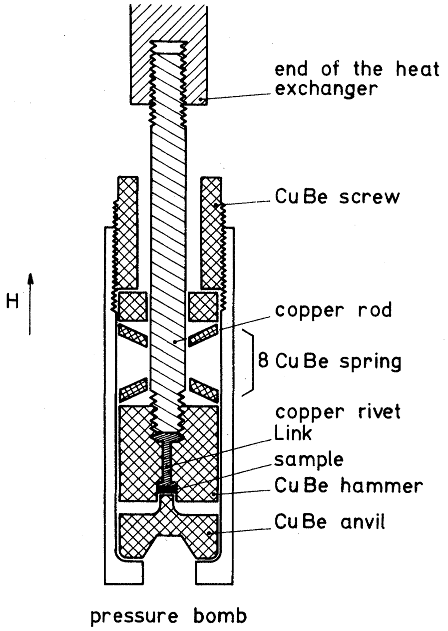

FIG. 1. Experimental arrangement for mounting the sample under pressure.

mize interconversion of the hexagonal and cubic phases, the proton beam intensity was kept low. The samples which were mounted in the high-pressure cell were in the form of disks, 1.2 mm in diameter and 0.1 mm thick (Fig. 1), the applied field being perpendicular to the faces of the disk.

The cell, with pressure already applied, was thermally attached to a chrome-alum salt slurry which was then cooled by adiabatic demagnetization. To overcome the poor thermal conductivity of the beryllium-copper cell walls, various arrangements were tried: electroplating the pressure anvils with copper, or mounting the sample with a copper rivet. In Fig. 1 we have shown the second method, which gave good thermal contact to the sample. The applied pressure was not measured directly in the cell; instead, it was calculated from the pressure applied to the anvils by a hydraulic press. Taking account of frictional losses in the press and the cell, one can estimate the difference of the pressures in the cell and in the hydraulic fluid to be about 25%; this effect is, however, partially compensated for at low temperatures by the increase in the value of Young's modulus for beryllium copper.[10] The pressures quoted are based on the fairly arbitrary supposition of a 20% reduction relative to the hydraulic pressure. After having performed auxiliary experiments using a Fe^{60}Co thermometer in place of the sample and a Au^{54}Mn thermometer on the thermal link to the salt slurry, in which it was verified that no appreciable thermal gradients were present, we chose a single crystal of Co^{60}Co soldered on to the end of the thermal link as a thermometer for the La^{137m}Ce measurements. We also took the precaution of applying a minimum pressure p_0 of 2 kbar. To investigate the reversibility of the applied pressure we performed a series of experiments on the same sample, first at the minimum pressure p_0, then at the maximum pressure of 10 kbar, then again at p_0, a process which was complicated by the short half-life of ^{137m}Ce (44 h).

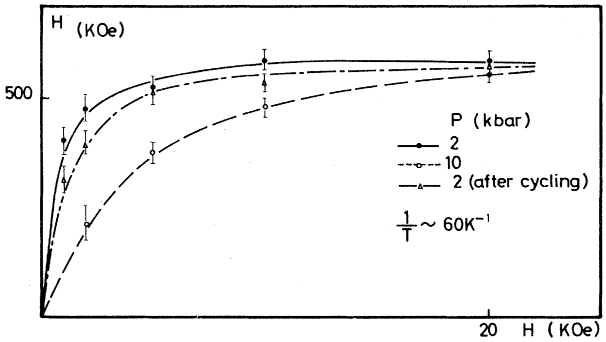

FIG. 2. Variation of the effective hyperfine field H_{eff} as a function of applied pressure and magnetic field at a given temperature.

The anisotropy of the 255-keV γ rays, accompanying the $M4$ transition in the ^{137m}Ce decay, was determined by using a Na(Tl)I scintillation detector and interpreted in terms of an effective hyperfine field H_{eff} in the usual way,[7] modified by the above analysis.

Figure 2, which represents the dependence of H_{eff} as a function of applied field H at $T^{-1} \simeq 60$ K^{-1}, shows clearly that the variations of the slope $(dH_{\text{eff}}/dH)_{H\to 0}$ are significant. The ratio of the initial slopes at 10 and 2 kbar leads to a T_K ratio of

$$T_K(10)/T_K(2) \sim 5,$$

and with the simplified hypothesis indicated above, the corresponding T_K's are

$$T_K(2) = 120 \text{ mK}, \quad T_K(10) = 600 \text{ mK}.$$

Since the variation in T_K is not accompanied by appreciable variation in the saturation hyperfine field $H_n(\text{sat})$, a purely ionic model seems sufficient to describe the cerium in the pressure range studied.

To analyze the results in greater detail we will consider the well-known model of a deep-lying virtual $4f$ bound state, that is, a $4f$ state whose energy $E(p)$ relative to the Fermi energy is somewhat greater than its width Δ. As was shown by Schrieffer and Wolff,[11] the impurity then obeys an ionic-type exchange Hamiltonian $-2\Gamma\vec{S}\cdot\vec{s}$ whose interaction strength Γ is related to Δ, E, and ρ, the density of states of the conduction electrons at the Fermi level, by

$$\Gamma = \Delta/\pi\rho E(\rho).$$

The low-field measurements determine the relative displacement of the $4f$ level, $\delta E/\Delta$, as a function of the pressure since T_{K} is related to Γ and ρ by

$$T_{\mathrm{K}} = T_{\mathrm{F}} \exp(-1/2\Gamma\rho)$$

which leads to a logarithmic variation,

$$\ln[T_{\mathrm{K}}(p)/T_{\mathrm{K}}(0)] = \tfrac{1}{2}\pi\ \delta E(p)/\Delta.$$

Supposing that $\delta E(p)$ varies linearly with pressure, one obtains $\delta E \sim 1.3\Delta$ for $\delta p \sim 10$ kbar.

The high-pressure measurements determine the minimal distance $E_{\min}(0)$ of the $4f$ level from E_{F} at zero pressure, even in the absence of precise knowledge of the hyperfine coupling and the nuclear moment of the isotope studied. Thus, in the Anderson picture, the change in H_n^{sat} with pressure is linked to $\delta E(p)$ and $E(0)$ by the relation

$$\frac{H_n^{\mathrm{sat}}(p) - H_n^{\mathrm{sat}}(0)}{H_n^{\mathrm{sat}}(0)} \sim \frac{\Delta}{\pi E^2(0)}\,\delta E(p).$$

Then $E_{\min}(0)$ is defined by the relative experimental accuracy ($\delta H_{\mathrm{eff}}/H_{\mathrm{eff}} \sim 5\%$) and by the low-field determination $\delta E/\Delta$:

$$E_{\min}(0) \sim -3\Delta.$$

The phase shifts δ_{F} at the Fermi level are thus larger than $\varphi_{\mathrm{F}\,\min} \sim 162°$. By comparing with the measurements of Sugawara and Yoshida[12] on *Y*Ce (with T_{K} larger than that for *La*Ce), which gave $\varphi_{\mathrm{F}\,\min} \sim 173°$, one can conclude that $E_{\min}(0)$ overestimates the true position $E(0)$ of the $4f$ state. The description of cerium by an ionic model, even in the limit of high T_{K} (100 K), is in agreement with the analysis of Hirst,[13] which was based on the observation that intra-atomic Coulomb correlations stabilize the effective charge on the cerium impurities.

A determination of $E(0)$ could also be made by using the analysis of Coqblin, Maple, and Toulouse,[5] which locates the maximum of $dR/d\ln T$ at $E(p) \sim 1.5\Delta$, leading to $E(0) \sim -3\Delta$ as a result of our determination of $\delta E(p)$ and the resistivity measurements of Kim and Maple.[3] But, in fact, Gey and Umlauf[4] have proved that a purely ionic model ($E/\Delta \gg 1$) and the expression obtained by Hamman in calculating the Kondo resistivity are sufficient to explain the maximum in $dR/d\ln T$.

In conclusion, our NO experiment is the first direct proof that the magnetic-nonmagnetic transition takes place well above 10 kbar for Ce in La. Finally, it should be emphasized that since our results are in good agreement with the analysis of superconductivity measurements[3] using the expression of Müller-Hartmann and Zittartz,[14] giving $T_{\mathrm{K}}(11)/T_{\mathrm{K}}(0) \simeq 10$, our experiments support the validity of the latter theory.

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