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Specific heat of $(Ce_{1-c}Gd_c)Rh_2$ compounds

R. Kuentzler
Institut de Physique et Chimie des Materiaux de Strasbourg, 67084 Strasbourg Cedex (France)

A. Tari*
Laboratoire Louis Néel, CNRS, 166X, 38042 Grenoble Cedex (France)

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Abstract

The series $(Ce_{1-c}Gd_c)Rh_2$ has been investigated by means of specific heat measurements. At the $CeRh_2$ end of the series the substitution of gadolinium for cerium reduces the γ value. At $c=0.12$ the system enters into a spin-glass-like magnetic phase. On further increasing the gadolinium concentration, long-range magnetic order is reached at about $c=0.25$.

1. Introduction

Cerium and its intermetallic compounds are in the class of so-called "abnormal" rare earths which are schematically classified as (i) the Kondo systems and (ii) the intermediate valence (IV) systems. In the IV systems, the rare earth atoms fluctuate between the $4f^n$ and $4f^{n-1}$ configurations which have comparable energies.

Most of the intermetallic compounds of cerium with the transition metals are in the class of the IV systems [1] where cerium has, on average, a non-integer number of 4f electrons. This is the result of the hybridization between the conduction electrons of the host and the 4f band of cerium and the difference in the properties of these compounds is closely related to the strength of this mixing. The hybridization therefore is expected to be particularly strong in the compounds with a high density of d electrons. This indeed appears to be the case [2, 3].

Recent L_{III} experiments carried out by Wohlleben and Rohler [4] and Mihalisin *et al.* [5] put the valency of cerium in $CeRh_2$ at between 3.13 and 3.21. From a high temperature susceptibility study, Weidner *et al.* [1] put an upper limit of 3.4 for the valency of cerium in $CeRh_2$ at 1200 K. Harrus *et al.* [6, 7] investigated the change in the valency of cerium in $(Ce, R)Rh_2$, $R \equiv La$, Y and $Ce(Rh_{1-c}Pt_c)_2$ by means of susceptibility, specific heat, resistivity

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*On sabbatical leave from King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.

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and lattice spacing measurements. In their specific heat study on Ce($Rh_{1-c}Pt_c$)$_2$ they found a value of 22.5 mJ Mol^{-1} K^{-2} for the coefficient γ of the electronic specific heat at the $CeRh_2$ end of the series. The variation of γ with the concentration of platinum showed a small initial decrease in the range $c \leqslant 0.2$. Above this concentration it showed a rapid rise, reaching 200 mJ mol K^{-2}; this indicates that this system goes from an IV state to a state approaching the heavy-fermion state as defined by a high γ value.

The series ($Ce_{1-c}Gd_c$)Rh_2 is expected to be interesting. The substitution of gadolinium for cerium leads to a number of effects [8]. From the viewpoint of the electronic specific heat, the most important effect, particularly at the $CeRh_2$ end of the series, is that resulting from the replacement of cerium with its strong hybridization tendency, by gadolinium with a well-localized 4f state. This should lead to the so-called "hybridization hole", namely a reduction in the density of the conduction electrons in the 5d band of the host and hence in γ, the coefficient of the electronic specific heat. This is indeed the case as will be shown in Section 3. Furthermore, the substitution of gadolinium will result in suppression of the spin fluctuation temperature at the neighbouring cerium sites, thereby driving these cerium atoms towards the magnetic Ce^{3+} state. Also, even in the region where the concentration of gadolinium is high, there will be some non-magnetic cerium atoms with fluctuating valency [8]. This should reflect itself strongly in the relaxation time of a resonance probe such as Gd^{3+} or ^{165}Ho in this series. We have therefore been studying the ($Ce_{1-c}Gd_c$)Rh_2 compounds by means of (i) magnetization and susceptibility, (ii) specific heat measurements and (iii) by the electron spin resonance of Gd^{3+} and (vi) the nuclear magnetic resonance of ^{165}Ho introduced as a dilute substitutional impurity. The results of the magnetic measurements have already been published [8] and those of the resonance studies will be published elsewhere. In this paper we report the results of the specific heat measurements.

2. Experimental details

Seven compounds with $c = 0.01$, 0.03, 0.10, 0.15, 0.30, 0.45 and 0.60 were made by melting together the stoichiometric amount of 99.99% pure rare earths and 99.9% pure rhodium. The constituents were melted together in a cold-crucible induction furnace at the Laboratoire Louis Néel, Grenoble, France, except for that with $c = 0.45$ which was made in a conventional arc furnace. All the samples were melted together and then remelted a minimum of four times for good homogeneity under a high purity argon atmosphere. There was almost no weight loss during the melt. The resulting buttons were then heat treated at 800 °C for 3 days under a vacuum of $p < 10^{-7}$ Torr. The cubic Laves structure of all the compounds was confirmed by conventional X-ray diffractometry which did not reveal any impurity phase.

The specific heat measurements were made automatically by a quasi-adiabatic method in the interval $1.5 < T < 20$ K. In some cases the measurements were extended up to 40 K. The temperature sensor was a Cryocal germanium resistor. An accuracy of better than 1% was achieved in the specific heat for materials of about 1 g mass, while our samples had a typical mass of about 5 g.

3. Results and discussion

The straightforward variation of the total specific heat C_t with temperature of the samples with $c=0.01$, 0.03, 0.10 and 0.15 is shown in Fig. 1. As the figure shows, the graphs of the compounds with $c>0.01$ do not extrapolate linearly to zero and show a broad hump at a certain temperature which increases with increasing gadolinium concentration. This is particularly clear in the case of the samples with $c=0.15$. This is one of the features seen in the spin glasses in which the initial slope of the C *vs.* T graph is weakly concentration dependent. Indeed the graphs of $c=0.10$ and $c=0.15$ samples start to merge at about $T=1.6$ K, indicating that the initial slopes of these two compounds are very similar. The compound with $c=0.01$ does not show the same behaviour as the remaining three compounds and, as the figure shows, its specific heat extrapolates to zero smoothly as $T\to 0$.

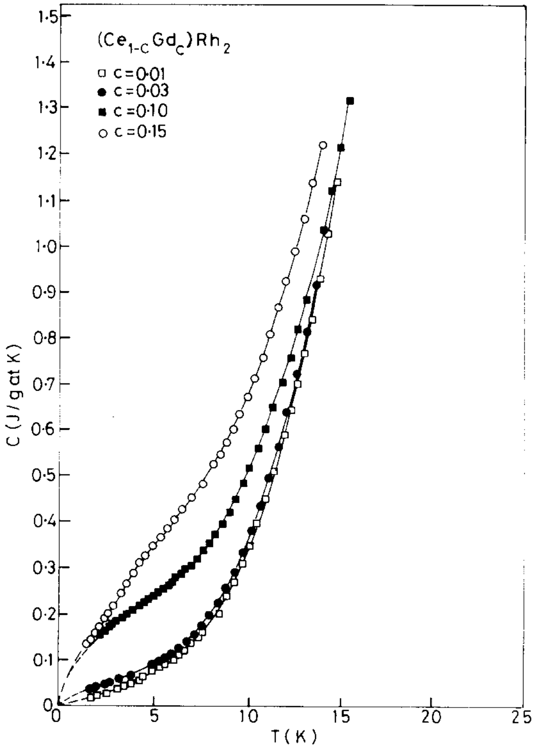

Fig. 1. Temperature variation of the total specific heat C_t of the compounds with $c\leqslant 0.15$.

The C/T *vs.* T^2 graphs of the above four compounds are shown in Fig. 2. A small anomaly is detectable at $T=5.5$ K in the graph of the sample with $c=0.01$. Although the X-ray investigation did not reveal any foreign phase, the most likely cause of this anomaly is an impurity phase and not experimental. This anomaly makes an accurate determination of γ for this compound somewhat difficult. Furthermore the C/T *vs.* T^2 graph of this sample is not linear at high temperatures. Therefore the values Θ_D and γ obtained for this compound have large uncertainties.

At the lowest temperatures, because of both the effect of statistical aggregation of gadolinium ions and the consequent presence of short-range order, and the approach of the alloys to the critical concentration for magnetism, the graphs show an upturn. Above this range the curves in Fig. 2 are well represented by

$$C=\gamma T+\beta T^3 \tag{1}$$

with

$$\gamma=\frac{(\pi k_B)^2 N(E_F)}{9} \qquad \beta=\frac{1943.74}{{\Theta_D}^3} \tag{2}$$

where γ and Θ_D refer to 1 g atom (1 g atom $=\frac{1}{3}$ mol). Here $N(E_F)$ is the total density of states of the conduction electrons and Θ_D is the low temperature Debye temperature.

The ordering temperatures of the samples with $c=0.15$ ($T^*=4$ K) and $c=0.30$ ($T_c=17$ K) [8] are within the temperature range of our measurements. As Figs. 1 and 2 show, no anomaly is observed at the ordering temperatures of these alloys.

The variation in C/T with T^2 for the compounds with $c=0.30$, 0.45 and 0.60 is shown in Fig. 3. It is evident from the figure that their low-temperature

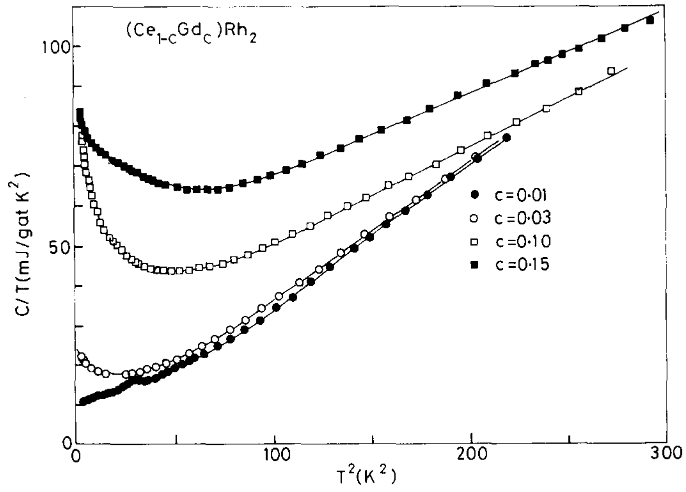

Fig. 2. C/T *vs.* T^2 representation of the compounds with $c \leqslant 0.15$.

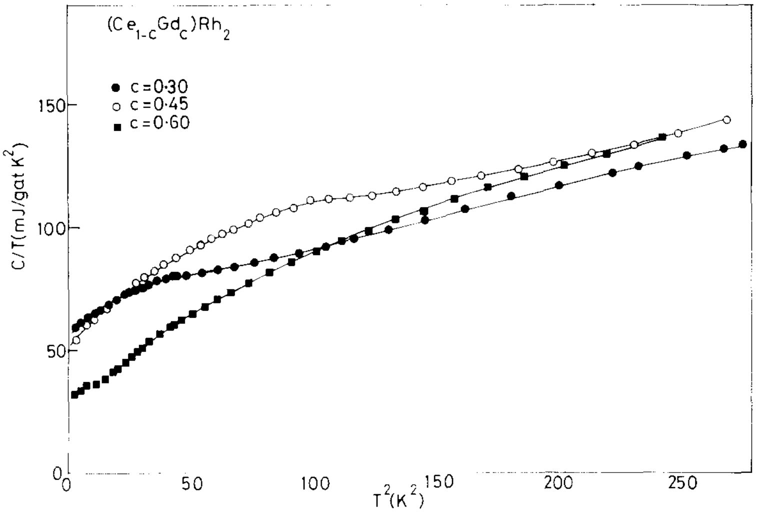

Fig. 3. C/T vs. T^2 graphs of the compounds with $c=0.30$, 0.45 and 0.60.

specific heat is dominated by a magnetic term. Also, at certain temperatures which are low compared with the Néel temperature T_N of the alloys, the curves show a broad maximum, the temperature of which increases with increasing gadolinium concentration. Similar broad structures have been observed in $(Gd_{1-c}Y_c)Cu_2$ [9]. In all cases the temperature of the maximae lie below about 30% of T_N of the alloys. These structures in the gadolinium intermetallics are now known to be due to a Schottky-like anomaly in the ordered state and are the result of the splitting of the $(2S+1)$-fold degenerate ground state of the gadolinium spin by the internal molecular field [10].

Although the value of γ for these concentrated compounds may be obtained from the very low temperature portion of the C/T vs. T^2 graphs, it is difficult to obtain their Θ_D temperatures and hence to isolate the magnetic term C_m in their specific heat. We have, however, attempted to calculate C_m for the sample with $c=0.30$.

For this purpose we chose $LaRh_2$ as host in preference to YRh_2 or $CeRh_2$ for the following reasons: lanthanum is neighbour to cerium in the periodic table and has a considerable 4f character in its 5d band. Furthermore it has the same outer electronic configuration as cerium while yttrium has none of these advantages. We therefore believe $LaRh_2$ to be a more appropriate host than YRh_2 for our purpose. The use of $CeRh_2$ is inappropriate as host because the substitution of gadolinium for cerium will reduce the density $N(E_F)$ of state, as has already been explained, leading to $\Delta\gamma<0$ at the $CeRh_2$ end of the series.

The density of states for $LaRh_2$ and hence its γ value may be estimated from its measured electronic susceptibility [11] $\chi=7.3\times10^{-5}$ emu mol^{-1} from which we compute $N(E_F)=2.2$ state eV molecule^{-1}. Using this value in (2) we obtain $\gamma=4.43$ mJ (g atom)$^{-1}$ K^{-2}. Although this is close to the

γ values measured for the dilute compounds of our series, it appears to be somewhat large. The susceptibility of $CeRh_2$ is 8.8×10^{-4} emu mol^{-1} [12] which is a factor of about 12 larger than that of $LaRh_2$ while its γ value is only twice that of $LaRh_2$, as we have just seen.

The value of Θ_D can reasonably be estimated from [13]

$$M_x\Theta_x^2 = M_y\Theta_y^2 \tag{3}$$

Using the values of M and Θ_D for the $Ce_{0.85}Gd_{0.15}Rh_2$ sample in (3) we calculated the value of Θ_D for the $Ce_{0.70}Gd_{0.30}Rh_2$ sample. We then computed the value of Θ_D for $LaRh_2$ normalized to that of the above sample [14] and found it to be 113 K. Using the values of γ and Θ_D thus obtained for $LaRh_2$, we have calculated C_{LaRh_2} and subtracted it from the total specific heat of the $Ce_{0.7}Gd_{0.3}Rh_2$ sample for each temperature and thereby obtained an estimated magnetic specific heat C_m for this compound. The curve thus obtained is shown in Fig. 4. This procedure appears to be meaningful for not only is the transition temperature obtained from this graph close to that obtained from magnetic measurements ($T_N = 17$ K) but also the curve indicates a very broad transition because of the inhomogeneity of magnetism in this compound, in agreement with the conclusion reached on the basis of magnetic measurements [8]. The entropy change at T_N is 3.75 J mol^{-1} K^{-1} while for this compound we would expect it to be about $0.3\,R\ln(2S+1) = 5$. However, part of the entropy lies under the broad maximum and hence the magnitude obtained is reasonable.

The values of Θ_D and γ are listed in Table 1 and the variation of γ with the concentration of gadolinium is shown in Fig. 5 where for the compounds with $c > 0.30$ the values of γ obtained from the lowest portion of the C/T

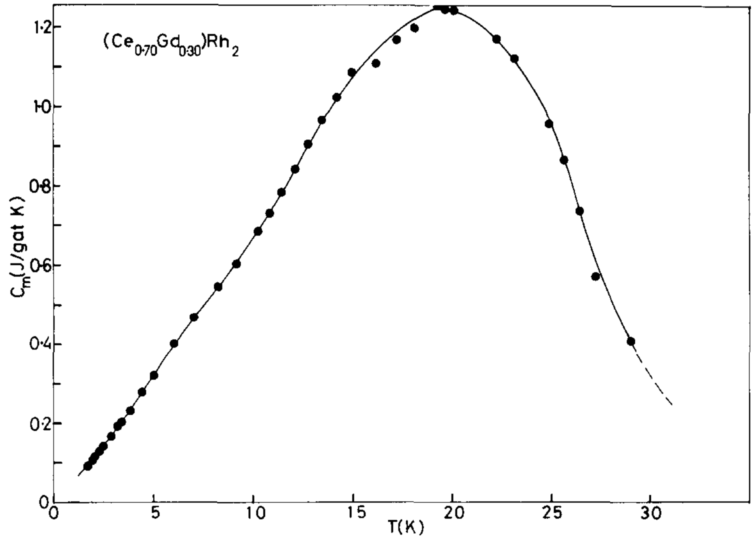

Fig. 4. Temperature variation of the "estimated" magnetic specific heat C_m for the compound with $c = 0.30$.

TABLE 1

Values of γ and Θ_D for the series $(Ce_{1-c}Gd_c)Rh_2$ (the samples with $c \geqslant 0.30$ contain 1 at.% Ho)

c	Θ_D (K)	γ (J (g atom)$^{-1}$ K^{-2})
0.00	–	7.5 [7]
0.01	184	5.0
0.03	185	5.5
0.10	201	23.0
0.15	212	47.5
0.30	–	59.0
0.45	–	53.0
0.60	–	25.5

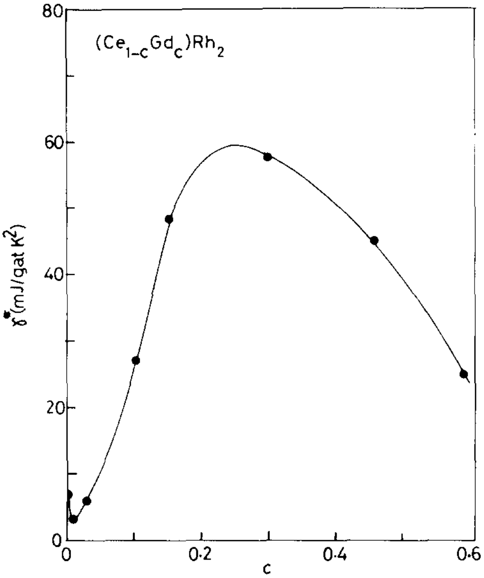

Fig. 5. Variation of γ with gadolinium concentration for the series $(Ce_{1-c}Gd_c)Rh_2$.

vs. T^2 graphs are used. For this reason we have used γ^* in the figure to indicate this fact. As the figure shows, the curve peaks at about $c = 0.25$. Unfortunately we do not have data for this interval to give the precise location of the peak.

From their magnetic study, Kariapper and Tari [8] concluded that this system makes a transition to long-range ferrimagnetic order at about $c = 0.30$. However, the present investigation shows that the critical concentration for long-range ordering is somewhat lower, at about $c = 0.25$ where γ^* reaches its maximum value. We note that the γ value for the compound with $c = 0.30$ is the highest among the compounds studied, in accordance with the conclusion reached by the above workers.

Another meaningful graph is that of the total specific heat at a fixed temperature against concentration. This is shown in Fig. 6 where we have plotted $C_t(1.7\ \mathrm{K}) - C_t(0.0\ \mathrm{K}) = C_t(1.7\ \mathrm{K})$ against gadolinium concentration. The graph peaks at about $c = 0.12$. This is the critical concentration for the appearance of magnetism in this series. Indeed the sample with $c = 0.15$ has a T^* of 4 K [8]. However, the magnetic phase is not ferrimagnetic but spin glass like. Figure 7 shows the temperature variation of the real part of the a.c. susceptibility $\chi'_{\mathrm{a.c.}}$ for this sample. As the figure shows, $\chi'_{\mathrm{a.c.}}$ goes through a maximum at about $T = 4$ K and is found to be frequency dependent. This and the fact that the initial slope of the *C vs. T* graphs of the compounds in this region is weakly concentration dependent leads us to conclude that the magnetic phase entered by this series at $c = 0.12$ has a predominant spin glass character.

Figure 5 shows that, at low gadolinium concentrations, γ decreases initially and, after going through a minimum at around $c = 0.02$, starts to increase as the gadolinium content is increased still further, reaching its peak value at about $c = 0.25$. At the $CeRh_2$ end of the series the decrease in value of γ with increasing c is anticipated. Here the substitution of cerium by gadolinium removes the contribution of the cerium atoms to the density of states through the 4f–5d hybridization and replaces it with the well-localised 4f band of gadolinium which has virtually no mixing with the conduction band. The same situation should exist in other IV systems such as $CeRu_2$ for which Sereni *et al.* [15] found a γ value of 64 mJ mol^{-1} K^{-2}. This value is larger by a factor of 3 than that found by Harrus *et al.* [7] for $CeRh_2$ and suggests that the density of states in $CeRu_2$ is considerably larger than that of $CeRh_2$ and hence a larger hybridization should be expected at cerium sites in $CeRu_2$. This should make the variation of γ with c even

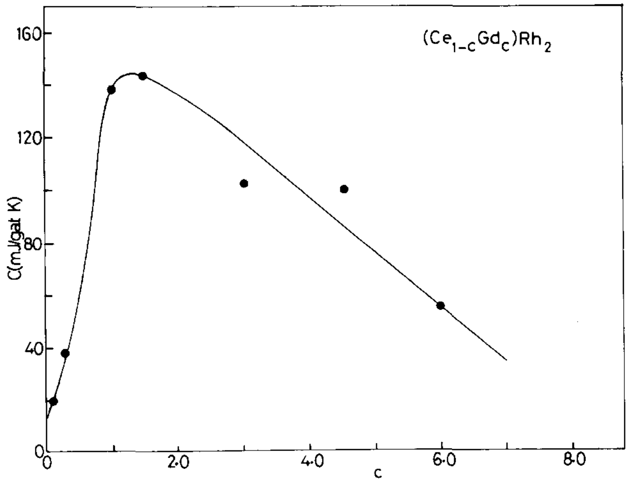

Fig. 6. Change in C_t (1.7 K) $-$ C_t (0.0 K) $=$ C_t (1.7 K) with gadolinium concentration.

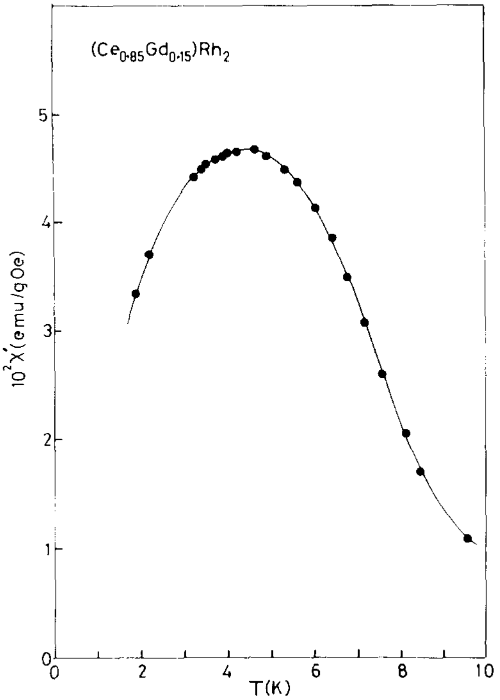

Fig. 7. Temperature variation of the real part of the a.c. susceptibility $\chi'_{a.c.}$ for the compound with $c = 0.15$. The measurements were made in an a.c. field of 2 Oe and a frequency of 158 Hz.

more pronounced except that the superconducting state below 6.3 K in this compound may make the situation somewhat complicated.

We interpret Figs. 5 and 6 as follows: cerium is in an IV state in $CeRh_2$. The substitution of gadolinium for cerium introduces localized moments at the gadolinium sites which act on their neighbouring cerium ions as an effective local field, thereby driving them towards the magnetic Ce^{3+} state. As the spin fluctuation temperatures of these ions approach zero, the contribution of the paramagnons at these sites become more and more important. At $c = 0.12$ a spin-glass-like magnetic phase is reached. Above this concentration a gradual long-range ferrimagnetic state sets in and the contribution of the local magnons to the specific heat becomes important. At about $c = 0.25$ the long-range ferrimagnetic order is reached where γ takes its maximum value. A further increase in the gadolinium concentration beyond $c = 0.25$ raises the ordering temperature of the alloys and consequently the number of magnons excited become fewer and fewer and hence their contribution to the specific heat decreases as observed.

4. Conclusion

We conclude that at the $CeRh_2$ end of this series the substitution of gadolinium for cerium reduces the γ value as a result of the reduction in the density of the 5d states at the cerium sites. At $c = 0.12$ the system enters a spin-glass-like magnetic phase. On further increasing the gadolinium content, long-range ferrimagnetic order is reached at about $c = 0.25$.

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