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A Whiff of Chemistry in Heavy Electron Physics

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RARE EARTH IMPURITIES IN YB_6 AND ZrB_{12}

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Abstract.—We present data on the depression of the superconducting transition temperatures of YB_6 and ZrB_{12} by rare earth impurities. These data show unusual features. Ce in YB_6 is in some ways analogous to Yb in ZrB_{12}, and this analogy also appears to hold between Ce in CeB_6 and YB in YbB_{12}.

This is a report on experiments concerned with rare earth impurities in the superconductors YB_6 and ZrB_{12}.

It has been found that an interaction of the form

$$H_{\text{int}} = -2J_{sf}\,\mathbf{S}\cdot\mathbf{s} \qquad (1)$$

can explain in a semiquantitative way a number of magnetic phenomena in metals dependent upon the interaction between 4*f* spins **S** and conduction electrons with spin **s**. J_{sf} gives the strength of the coupling and is roughly constant across the rare earth series. Of interest here is that Hamiltonian (1) predicts that the depression (ΔT_c) of the transition temperature of a superconductor by localized spins will vary as

$$\Delta T_c \propto J^2{}_{sf}\,S(S+1)n \qquad (2)$$

for small impurity spin concentration n.[1] For strong spin-orbit coupling, the spin factor $S(S + 1)$ is replaced by $(g - 1)^2 J(J + 1)$, where J is the total angular momentum of the localized spins and g the Landé g-factor.

There are thought to be two principle contributions to J_{sf}: a ferromagnetic part arising from the Coulomb exchange integral and an antiferromagnetic part present when the 4*f* electrons occupy a virtual bound level. For the latter case, the magnetism varies roughly as the reciprocal of the 4*f*-Fermi level energy difference.

Figure 1 shows the depression of the superconducting transition temperature of YB_6 with 1 atomic per cent addition of rare earth for Y. The dashed curve shows the variation of $S(S + 1)$, the solid curve $(g - 1)^2 J(J + 1)$ across the series. Both curves are normalized for the depression of Gd impurities.

For the most part the depressions follow the trend of $(g - 1)^2 J(J + 1)$. This indicates that Hamiltonian (1) with J_{sf} constant across the series can describe the local moment-conduction electron interaction. Eu, Yb, Tm, and Ce additions deviate from this behavior. We observe that EuB_6 and YbB_6 are known to contain divalent Eu and Yb. In YB_6, it is not known in what $4f$ configuration these elements are present; Yb replacements for Zr or Y have a larger effect than expected for either an f^{13} or an f^{14} configuration. Even assuming electrons are removed from the conduction band, the effect is still larger than ex-

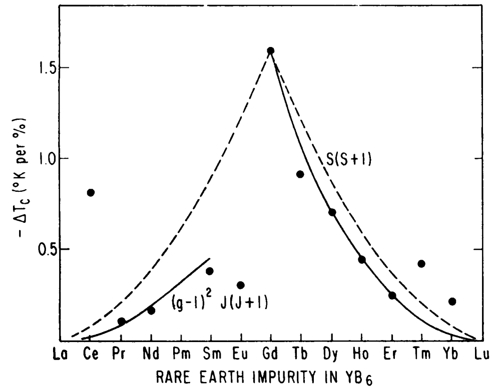

FIG. 1.—Depression of the superconducting transition temperature of YB_6 by 1 atomic per cent addition of rare earth for Y.

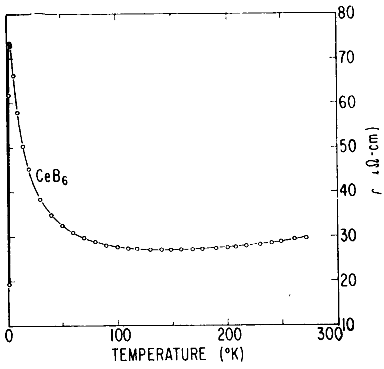

FIG. 3.—Temperature dependence of the electrical resistivity of CeB_6.

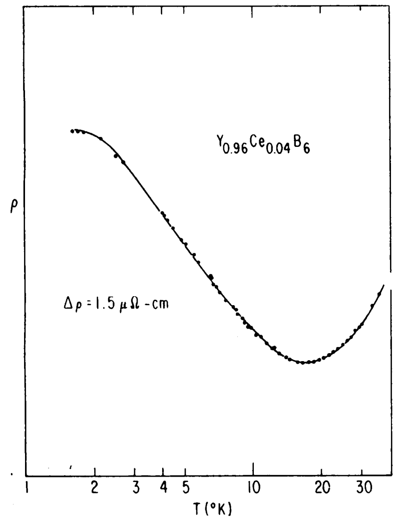

FIG. 2.—Electrical resistance of $Y_{0.96}Ce_{0.04}B_6$ plotted against log T. The abscissa is labeled with temperatures in °K. The ordinate zero is arbitrary; the depth of the minimum is 1.5 $\mu\Omega$-cm, which is roughly 10% of the residual resistivity.

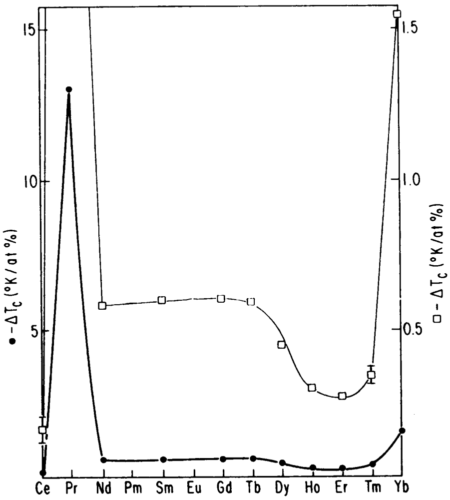

FIG. 4.—Depression of the superconducting transition temperature of ZrB_{12} by 1 atomic per cent addition of rare earth for Zr. The squares refer to the right-hand scale and are an expanded version of the data represented by the circles (*left-hand scale*).

pected using a simple BCS model. The large dependence for *Tm* is equally puzzling.

The large effect of Ce additions suggests the presence of a virtual 4*f* level. Figure 2 shows a plot of the electrical resistance versus log T for $Y_{0.96}Ce_{0.04}B_6$. The presence of the minimum at low temperatures is consistent with J_{sf} being antiferromagnetic, according to Kondo's theory.[2] In this connection it is interesting to note that this minimum also exists in CeB_6 as shown in Figure 3. The sharp drop near 3° appears connected with antiferromagnetic ordering. Below about 0.5°K, the resistance flattens out (this is not shown). It is tempting to suppose that the cause for the resistance rise at low temperatures is similar in the two cases.

Figure 4 shows the depression of the superconducting transition temperature of ZrB_{12} by 1 atomic per cent addition of rare earth for Zr. These data excepting the Yb point were reported previously.[2] It was argued then that the exceedingly large effect of Pr was due to a virtual bound f^2 configuration, due to the high pressure exerted on the Pr substitutions by the Zr host lattice. Here we confine our attention to the situation with respect to Yb. We have not detected any electrical resistance minimum in ZrB_{12} containing Yb impurities above 2°K, to an accuracy of about 0.3 per cent of the residual resistivity of the material. Since the temperature at which such a minimum occurs is a very strong function of J_{sf}, virtual level contributions are not ruled out. Minima for Pr impurities in ZrB_{12} occur around 35°K.

To investigate this situation further, Yb was added to ScB_{12}. As a first approximation it can be imagined that the effect of replacing Zr by Sc in ZrB_{12} is to lower the Fermi level, Sc having one less valence electron than Zr. Figure 5 shows the resistance of $Sc_{0.95}Yb_{0.05}B_{12}$ (approximate composition). Now there is a very deep minimum present. A sample at ~20 per cent Yb has a resistance which even increases on cooling below room temperature.

In this connection the resistance behavior of YbB_{12} is of interest. This phase is difficult to prepare. We have only succeeded in obtaining a mixture of 60 per cent YbB_{12}-40 per cent YbB_6. The lattice constant YbB_{12} indicates that Yb is trivalent in this compound. The resistance of the mixture increases nearly two orders of magnitude of cooling from 300° to 2°K.

As mentioned in passing, YbB_6 in which Yb is divalent should be a semi-

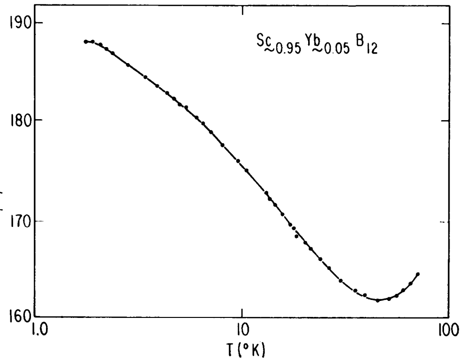

FIG. 5.—Electrical resistance of $Sc_{\sim 0.95}$-$Yb_{\sim 0.05}B_{12}$ plotted vs log T. Several temperature values are indicated. The minimum is near 45°K. The X-ray data was not sufficiently accurate to fix the composition. The Yb concentration, assuming no weight loss (unlikely) of Yb in preparation, is 8 at atomic per cent.

conductor. Specific heat measurements show the electronic specific heat gamma to be very small.[4] A sample we have prepared containing (from X-ray patterns) about 90 per cent YbB_6 with 5 per cent each of YbB_4 and YbB_{12} had a resistance ratio at 4°K of 0.8.

Supposing that YbB_{12} is a metal, then in the 60% YbB_{12}-40% YbB_6 sample, the semiconductivity would be short circuited by the metal. It appears, therefore, that YbB_{12} in pure form would have a highly unusual resistance behavior. We hypothesize that YbB_{12} is the virtual *f*-hole analog to CeB_6.

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