ductivity at the right-hand end of the transition metal series is not clear at present.

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<sup>13</sup>It has been independently suggested by Bucher, Brinkman, Maita, and Williams that  $q$ -dependent exchange may play a role in reducing the predicted mass enhancement (see Ref. 3).

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 $^{15}$ Since a set of well-localized Wannier functions (1) will in general depend on both  $k$  and  $\alpha$ , even the onecenter terms will be momentum dependent. These effects can further reduce the mass enhancement and increase the range of  $\chi(r)$ . See J. R. Schrieffer, to be published.

## NUCLEAR RELAXATION IN SUPERCONDUCTING NIOBIUM NEAR THE UPPER CRITICAL FIELD

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Up to now most nuclear-relaxation-time measurements in the mixed state of Type-II superconductors have been made far below the upper critical field  $H_{c2}$ . Their interpretation generally involves the well-known BCS behavior.<sup>1</sup> We report here  $T_1$  measurements in pure niobium near  $H_{c2}$ . The new point is essentially that in this region the distance between vortices becomes comparable with the coherence length. This is a gapless situation,<sup>2</sup> which gives rise to new features in the nuclear relaxation.

 $T<sub>1</sub>$  was measured in two different samples of niobium powder with average particle of 15  $\mu$ . We label them Nb I and Nb II. The upper critical fields at zero temperature are, respectively,  $H_{c2I}$ =8.2 kG and  $H_{c2II}$ =12.1 kG, as

determined by extrapolating the variation of  $H_{c2}$  vs T. By using the theoretical electron mean free path dependence<sup>3</sup> of the upper critical field of a Type-II superconductor, the ratio of the coherence length  $\xi_0$  to the mean free path *l* is found to be  $\xi_0/l = 0.7$  for Nb I and  $\xi_0/l$ = 1.5 for Nb II. Thus it turns out that sample I is rather clean, while sample II is rather dirty, though the  $\xi_0/l$  parameters differ by only a small factor. Most of the  $T_1$  measurements were done at temperatures between 1.4 and  $4.2\text{°K}$ , in magnetic fields from 3 to 9 kG (namely  $0.15 \le T/T_c \le 0.45$  and  $0.4 \le H/H_c 2 \le 1$ ).  $T_1$ was measured at the center of the nuclear magnetic resonance line in the following way: We saturated the thermal- equilibrium nuclear mag-

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netization by a few tens of 90' pulses (typically a <sup>60</sup> 6 rotating rf field was used). Then we observed the time recovery of the magnetization by the variation of the height of either a spin echo or a free precession. The latter was often unobservable due to the inhomogeneous line broadening in the presence of vortices. In most cases the recovery was found to be exponential due to the complete saturation that was achieved.

Some experimental values of  $T_1$  in Nb I are shown in Fig. 1. In the mixed state the temperature variation of  $T_1$  is clearly shown to be intermediate between the Korringa law and the BCS law. Furthermore, near  $H_{c2}$  and at low temperature this figure shows a rather rapid increase of  $T_1$  just below the transition temperature. Similar features are found in the  $T_1$  variation in Nb II, except that the increase near  $H_{c2}$  is not as sharp as in Nb I. From these experimental values we were able to plot the variation of the relaxation rate  $R = 1/T_1$  against the magnetic field, at a fixed temperature. The interesting parameter is the initial slope  $\left| d(R_S/R_N)/dH \right|_{H^{\pm}H_C, 2},$  where  $R_S$  and  $R_N$  are the superconducting and the normal state relaxation rates. The variation of the slope as a function of temperature is shown in Fig. 2.



FIG. 1. The nuclear relaxation time of  $Nb^{93}$  is plotted for sample Nb I vs  $T_c/T$ . The figure reproduces the experimental results for only six magnetic field values. The solid line shows the theoretical BCS law for  $T_c = 9.2$ °K. The dotted line represents the Korringa law $T_{1}\ensuremath{T}=380$  msec °K which is well fitted by the experimental points taken in the normal state (9400 0). The vertical dashes crossing the dotted line indicate the critical temperature corresponding to the fields in which  $T<sub>1</sub>$  was measured. These temperatures were determined independently.

The qualitatively different behavior of the two samples is apparent. For Nb I the slope varies approximately as  $log T$ . For Nb II the slope remains constant at low temperature. Thus for a small variation of mean free path close to the coherence length, the behavior of  $T<sub>1</sub>$ changes rapidly.

These results can be understood physically in the following way:  $R_S$  can still be described by a formula similar to the BCS equation involving a product of a squared density of states  $N^2(\epsilon)$  by a coherence factor. At low temperature  $T \ll T_c$  the energies  $\epsilon$  involved are small,  $\epsilon \simeq kT$ . The coherence factor is slightly larger than unity and  $N(\epsilon)$  is smaller than in the normal state. This dominates the behavior and leads to a relaxation rate smaller than in the normal state, in agreement with our results

In the dirty limit  $l \ll \xi_0$  the slope at zero temperature is finite and is given by the formula

$$
\frac{1}{R_N} \frac{dR_S}{dH} \bigg|_{\substack{H = H_{C2} \\ T = 0}} = 0.18 \frac{ec}{\sigma} \frac{1}{k_B T_c} \frac{1}{\beta |2K_2^2 (T = 0) - 1|}
$$

Here  $\sigma$  is the conductivity and  $K_2$  is given by the slope of the magnetization curve.<sup>5</sup> For Nb II, which is rather dirty, this formula gives  $8\times10^{-4}$  G<sup>-1</sup> to be compared with the experimen tal value of  $3.3 \times 10^{-4}$  G<sup>-1</sup>.

In the clean limit  $l \rightarrow \infty$ ,  $N(\epsilon)$  is known to diverge logarithmically as  $\epsilon$  vanishes. This implies a logarithmic divergence of the slope of  $R<sub>S</sub>$  at  $H<sub>c2</sub>$  for  $T \rightarrow 0.6$  The much larger slope in the cleaner sample Nb I supports this theoretical prediction.



FIG. 2. The initial slope of  $R_S/R_N$  just below  $H_{c2}$ is plotted versus T. The arrow at  $0.6T_c$  shows the theoretical temperature, at which the inversion of the sign of the slope is predicted.

Our samples do not strictly belong to either of the above limiting cases. In principle er of the above fimiting cases. In principle<br>we should use a more general analysis,<sup>7</sup> but the accuracy of our results does not justify it. We have made a simple numerical estimate of the ratio (slope Nb I)/(slope Nb II) at low temperature using Ref. 7 and assuming that  $K_2(T=0)$  is the same for both samples. We gind a ratio of 2:5. This agrees with the experimental low-temperature ratio taken from Fig. 2. At  $T = 0.6T_c$  the slope is predicted to pass through zero and to become negative for  $T > 0.6T_c$ . This important feature seems to be verified by extrapolation of the experimental points of Fig. 2. Further experiments are on the way to clarify this problem. In conclusion our experiments are in agreement with the theoretical results in the gapless region close to the upper critical field  $H_{c2}$ . In particular they show the predicted differences in behavior between the clean and the dirty limits.

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## MAGNETIC POLARIZATION OF A SINGLE MAGNETIC IMPURITY IN METALS

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The spin polarization of a single magnetic impurity in a metal in an external magnetic field has been calculated by variational method. The results are in agreement with the measurement of the hyperfine field by the Mössbauer technique.

Recently, there has been much interest in the nature of the ground state of dilute alloys of transition elements in some metals.<sup>1-4</sup> It is believed that below a Kondo temperature  $T_K$ , a bound state between the localized magnetic impurity and the conduction electrons is formed. This state has a binding energy of the order of  $kT_K$  and is characterized by a long-range conduction-electron polarization cloud.<sup>1</sup> There is experimental evidence that  $t$  this state is a singlet,<sup>3</sup> although the theoretic  $t$ . cal situation is not entirely clear. It had been expected that this bound state will partially break up in the presence of an external magnetic field and that it will completely dissociate when the external field reaches a value are when the external field reaches a value<br> $\mu_B H_K \simeq kT_K$ .<sup>3</sup> However, Frankel <u>et al</u>.<sup>4</sup> recent ly reported results of Mössbauer experiments on dilute Fe in Cu which shows that the bound state is not completely destroyed until an external field four to five times  $kT_K$  is applied. In this paper, we present results of calculations of a single magnetic impurity in an external field.

Our method is a variational approach similar to that of Heeger and Jensen' for the corresponding problem in the absence of the magnetic field. Our results are in agreement with the data of Frankel et al.<sup>4</sup>

We assume a one-orbital impurity, an antiferromagnetic s-d interaction, a large intraatomic Coulomb interaction so that the impurity is never doubly occupied, and the equality of  $g$  factor of the  $d$  electron and of the con-