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CALT-822-108

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 $T_{\text{KONDO}} > T_c$

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FEBRUARY 1979

A REPORT ON RESEARCH CONDUCTED
UNDER CONTRACT FOR THE
DEPARTMENT OF ENERGY

W. M. KECK LABORATORY OF
ENGINEERING MATERIALS

CALIFORNIA INSTITUTE OF TECHNOLOGY

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by

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Department of Energy Report No. 95, under Contract No. EY-76-C-03-0822.
Professor W. L. Johnson, principal investigator.

February 1979

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ABSTRACT

Measurements of upper critical field as a function of temperature and Fe-concentration are reported for the amorphous superconductors $((\text{Mo}_{.6}\text{Ru}_{.4})_{.80}\text{G}_{.20})_{1-c}\text{Fe}_c$, where G is a glass-former. The linear shapes of the H_{c2} vs. T curves near T_c agree well with predictions made by Matsura, Ichinose, and Nagaoka, for $T_{\text{Kondo}} \gg T_c$.

INTRODUCTION

The superconducting properties of amorphous $(\text{Mo}_x\text{Ru}_{1-x})_{80}\text{G}_{20}$ (where G is P or B) have recently been reviewed.^{1,2} The small coherence length ξ and large penetration depth λ characteristic of amorphous superconductors result in large values of H_{c2} , generally larger than those predicted by the dirty-superconductor theory of Maki.³ When doped with a magnetic impurity such as Fe, T_c is depressed, but the shape of the H_{c2} vs. T curve is unchanged. The predictions of Müller-Hartmann, Zittartz^{4,5} and of Schuh and Müller-Hartmann⁶ (MHZ) and of Matsuura, Ichinose, and Nagaoka (MIN)^{7,8} for Kondo-effect superconductors are discussed as they apply to these data.

The MIN theory is based on the different properties of magnetic impurities above and below T_{Kondo} in normal metals. When $T \gg T_K$, the impurities act like magnetic impurities in normal materials and have a pair-breaking effect in superconductors due to magnetic scattering. For $T \ll T_K$, the magnetic moment becomes compensated, the impurities are nonmagnetic in normal materials, the pair-breaking effect vanishes, and instead an effective repulsive interaction arises between paired electrons with energy $\epsilon < T_K$ due to virtual polarization of impurities, as pointed out by Sakurai.⁹ Between the two regions, for $T \sim T_K$, the pair-breaking interaction and effective repulsion cannot be separated and numerical methods must be used to interpolate between them.

The MHZ approach uses only the temperature dependence of the pair-breaking parameter in the Nagaoka-Suhl approximation, which MIN claim is inappropriate for $T_c < T_K$, based on the properties of normal Kondo materials. Schuh and Müller-Hartmann⁶ state that the deficiencies in

the MHZ theory are due to artifacts of the calculation and that their recent self-consistent pair-breaking calculation overcomes the earlier problems without considering a separate low-temperature pair-breaking mechanism. Previous experimental work on $\text{La}_{.8}\text{Th}_{.2}\text{Ce}$ ¹⁰ and $(\text{LaCe})\text{Al}_2$ ¹¹ by Maple, Fertig, et al., and by Riblet and Winzer¹² dealt with $T_K < T_C$ and has supported the MHZ theories. Recently, Takeuchi and Masuda¹³ used a wide range of $\text{La}(\text{Ce})\text{Sn}_{3-x}\text{Pb}_x$ and $\text{La}_{1-y}\text{Y}_y(\text{Ce})$ alloys to explore both $T_C > T_K$ and $T_C < T_K$ in the same families of materials. For the suppression of T_C with impurity content and for the jump in specific heat at T_C , their data fell between the values predicted by MHZ and MIN. One major problem with the comparison is the determination of T_K , since the definition used by MIN cannot be directly compared with experimental values. Since $T_K > T_C$ for the Fe-doped $(\text{Mo}_{.6}\text{Ru}_{.4})_{80}\text{G}_{20}$ amorphous alloys, the MIN and MHZ theories can be tested where their disagreement is strongest.

The multiple pair-breaking theory of Fulde and Maki¹⁴ combines the effect of spin depairing by scattering of conduction electrons by paramagnetic impurities with the momentum depairing from the penetration of the external field into the superconductor. Their scaling predictions for the spin pair-breaking parameter as a function of H_{c2} and impurity concentration can also be tested with these data over a large range of c .

EXPERIMENTAL PROCEDURES

The alloys were prepared by induction melting on a silver boat under an argon atmosphere. Amorphous foils were produced by rapid quenching using the "piston and anvil" technique.¹⁵

The structure of each sample was checked by x-ray scanning with a Norelco diffractometer (Cu-K α radiation). Several samples from each group were also examined by electron microscope and electron diffraction. Representative diffraction patterns and electron micrographs, as well as x-ray studies, have been published elsewhere.¹ The (Mo_{.6}Ru_{.4})₈₀P₁₀B₁₀ group of alloys was studied more extensively than the (Mo_{.6}Ru_{.4})₈₀P₂₀ group since homogeneous amorphous foils of the PB alloy were easier to produce than those of the P alloy. The [(Mo_{.6}Ru_{.4})_{.80}G_{.20}]_{1-c}Fe_c alloys were prepared by diluting the host material with c = .012 alloy.

Superconducting transition temperature (T_c) was measured using an AC-susceptibility bridge. Upper critical field (H_{c2}) was determined as described earlier¹⁶ by measuring resistance as a function of temperature in a fixed field. The shapes of the H_{c2} vs. T curves did not change significantly if $R = .1R_0$, $R = .5R_0$, or $R = .9R_0$ was used as the criterion for T_c . $H_{c2}(T)$ throughout this paper refers to the $R = .5R_0$ point. $T_c(H = 0)$ as determined by linear extrapolation of the H_{c2} curves was in good agreement with T_c determined using the AC bridge.

Magnetic susceptibility was measured as a function of field and temperature for several MoRuG-Fe alloys from T_c to 100 K using a Faraday apparatus in order to determine the moment carried by the Fe in the alloy, which is $0.5 \pm 0.2 \mu_B/\text{Fe atom}$. The Kondo temperature was determined by measuring the resistance in a 70 kG field to suppress the superconductivity and the effects of superconducting fluctuation phenomena. The Kondo temperature so determined must be corrected for magnetic field effects as discussed in ref. (17).

RESULTS AND DISCUSSION

The depression of T_c as a function of Fe concentration for the $(\text{Mo}_{.6}\text{Ru}_{.4})_{80}\text{P}_{20}$ and $(\text{Mo}_{.6}\text{Ru}_{.4})_{80}\text{P}_{10}\text{B}_{10}$ alloys is shown in Fig. 1 and 2. The Abrikosov-Gor'kov curve (AG)¹⁸ is shown for comparison, where the critical concentration n_{cr} is .0117 for the former and .0116 for the latter, as determined by fitting the data near T_c to the asymptotic form of the AG curve. The MIN and MHZ curves are not shown, since there are many possible choices of function, depending on the choice of t_k , the reduced characteristic temperature, T_k/T_{co} , where T_{co} is T_c for the undoped alloy.

The Kondo temperature is ~ 15 K, below which the resistivity in high field rises logarithmically, as shown in Fig. 3. The corresponding H_k is then ~ 225 kG which satisfies the condition that $H_{c2} < H_k$. MIN point out that their definition of the Kondo temperature makes it difficult to compare theoretical and experimental values because of an ambiguity in the approximation used. Although t_k for these data is ~ 3 , it is thus reasonable to compare it to their predictions for $1 < t_k < 100$. The normalized impurity concentration $\bar{n}$ used by MIN is

$$n = \frac{c}{(2\pi)^2 T_{co} \rho}$$

where ρ is the density of states of conduction electrons per atom, per spin. If $\rho = .53 \pm .05$ states/ev atom spin as determined by susceptibility measurements¹, then t_k must be ~ 300 . Since MIN use an s-d interaction and since superconductivity in MoRu alloys involves pairing of d-electrons, the direct use of ρ is not appropriate. For $T_c = 6\text{K}$, if t_k

Fig. 1. T_c as a function of Fe concentration c in $[(\text{Mo}_{0.6}\text{Ru}_{0.4})_{0.80}\text{P}_{0.20}]_{1-c}\text{Fe}_c$. The Abrikosov-Gor'kov curve (---) (AG) and a straight line (—•—•—) are shown for reference only.

Fig. 2. T_c as a function of Fe concentration c in $[(\text{Mo}_{0.6}\text{Ru}_{0.4})_{0.80}\text{P}_{0.10}\text{B}_{0.10}]_{1-c}\text{Fe}_c$. The Abrikosov-Gor'kov curve (---) (AG) and a straight line (-.-.-) are shown for reference only.

Fig. 3. Resistivity vs. temperature in 70 kG field for $c = .008$.

The smooth curve is a fit of the data to the form

$$R = a - b \ln(T/\Delta), \Delta = 15K \pm 2K.$$

were 10, then ρ would be 4.18 states/ev atom spin and if t_k were 100, then ρ would be 1.34 states/ev atom spin.

The upper critical field vs. temperature is shown in Fig. 4 for six iron concentrations. If $(\text{Mo}_{.6}\text{Ru}_{.4})_{80}\text{P}_{10}\text{B}_{10}$ behaves like a dirty-limit superconductor³, then $H_{c2}(T = 0, c = 0)$ would be 105 kG. In the normalized units of MIN, then

$$\left. \frac{d(H_{c2}/H_{c2}(0,0))}{d(T/T_{c0})} \right|_{T_c} = 1.47 \pm .03$$

for $c = 0 - 0.008$ and $1.63 \pm .03$ for $c = 0.010$, in good agreement with the MIN values of 1.45 for low c and 1.65 for high c , with t_k equal to either 10 or 100. For $t_k = 1$, the calculated initial slopes of the H_{c2} vs. T curves are not parallel, and they vary from 1.47 for $c = 0$ to 0.70 for $c = 0.01$, in contradiction to these data.

Earlier work¹⁶ has shown that amorphous superconductors do not follow a dirty superconductor H_{c2} vs. T curve, but rather a more nearly linear behavior to $T = .5T_c$ ($H = 0$) or less. Thus, H_{c2} near $T = 0$ has not yet been measured. The value used for H_{c2} may be somewhat low, and the comparisons of experimental and theoretical values of $(dH_{c2}/dT)_{T_c}$ may be fortuitous. No matter what value is chosen for $H_{c2}(0)$, however, the curves for $c < 0.01$ will have the same slopes, in contrast to the MHZ curves.

Schuh and Müller-Hartmann⁶, show that for all t_k , H_{c2} is not linear near T_c , and for all c , the H_{c2} vs. T curves are not parallel. Their predictions are in good agreement with the data of Fertig, Maple, et.al.^{10,11} for $t_k = 0.11$ where Schuh and Müller-Hartmann and MIN use

Fig. 4. H_{c2} as a function of T and c . Note that dH_{c2}/dT is $25.4 \text{ kG}/^\circ\text{K}$ for $0 \leq c \leq .008$, and $28.5 \text{ kG}/^\circ\text{K}$ for $c = .01$.

the same pair-breaking mechanism. For these data, where $t_k \sim 3$, there is agreement only with MIN, lending further support to their claim that the Suhl-Nagaoka approximation used by MHZ is invalid for $t_k > 1$.

Fulde and Maki¹⁴ predict that

$$c^{-1} \left(\frac{\alpha}{\alpha_{cr}} \right)_{imp} = A - B \ln [(T/T_c)^2 + \theta^2]^{1/2}$$

where $\left(\frac{\alpha}{\alpha_{cr}} \right)_{imp}$ is the effect of spin depairing due to scattering of

conduction electrons by paramagnetic impurities and can be calculated using

$$\left(\frac{\alpha}{\alpha_{cr}} \right)_{imp} = \frac{H_{c2}(0,T)}{H_{c2}(0,0)} - \frac{H_{c2}(c,T)}{H_{c2}(0,0)} - \frac{P}{P_{cr}}$$

where P/P_{cr} is the Pauli term due to polarization of the conduction band by the exchange field of the Fe spins. The expression

$\frac{1}{c H_{c2}(0,0)} (H_{c2}(0,T) - H_{c2}(c,T))$ should scale with $\ln T$. These data, when

scaled according to the prescription, give $\frac{1}{c} \left(\frac{\alpha}{\alpha_{cr}} \right)_{imp}$ scattered between

.8 and 1.10 with no scaling relationship apparent. Because the low field data are as widely scattered as the rest, it is not possible to conclude that the large fields used to study $(Mo_{.6}Ru_{.4})_{80}P_{10}B_{10}Fe$ alloys have changed the temperature dependence of $(\alpha/\alpha_{cr})_{imp}$.

CONCLUSIONS

The change in the behavior of $(Mo_{.6}Ru_{.4})_{80}G_{20}$ amorphous superconductors

with the addition of magnetic impurities is described well by MIN, at least near T_c , where $dH_{c2}(c,T)/dT$ for various c are nearly parallel. The failure of both the MHZ and Fulde-Maki theories, to predict this behavior lends more support to the MIN approach, considering that the Kondo-like properties of the impurities separately above and below T_c . Lower temperatures and higher fields are needed to study $H_{c2}(c,0)$ since the shapes of the reentrant curves are easily distinguished in the MIN and MHZ predictions. Further extension of this work to the case where $T_K < T_c$ is also of interest. In this limit, reentrance phenomena are possible. It would be worthwhile to examine the problem of reentrance in amorphous superconductors owing to the short coherence length ξ previously referred to. The statistical fluctuation of magnetic impurity concentration in a volume characterized by dimension ξ leads to intrinsic broadening effects in the superconducting phase transition. This in turn should lead to a rather interesting reentrant behavior.

ACKNOWLEDGEMENT - The authors thank Professor Pol Duwez for many fruitful discussions.

REFERENCES

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1. W. L. Johnson, 24th Conf. Magnetism and Mag. Mater., 1978, to be published; W. L. Johnson, Rapidly Quenched Metals III, V.2, p. 1 (The Metals Society, London, 1978).
2. W. L. Johnson, S. J. Poon, J. Durand, and P. Duwez, Phys. Rev. B 18, 206 (1978).
3. K. Maki, Physics 1, 21 (1964); K. Maki, Phys. Rev. 148, 362 (1966).
4. E. Müller-Hartmann and J. Zittartz, Phys. Rev. Letters 26, (1971).
5. E. Müller-Hartmann, Magnetism, V. 5, p. 353, ed. by H. Suhl (Academic Press, 1973).
6. B. Schuh and E. Müller-Hartmann, Z. Physik B 29, 39 (1978).
7. T. Matsuura, S. Ichinose and Y. Nagaoka, Prog. Theor. Phys. 57, 713 (1977).
8. T. Matsuura, Prog. Theor. Phys. 57, 1823 (1977).
9. A. Sakurai, Physica 86-88B, 521 (1977).
10. W. A. Fertig and M. B. Maple, Solid State Commun. 23, 105 (1977).
11. M. B. Maple, W. A. Fertig, A. C. Mota, L. E. DeLong, D. Wohlleben, and R. Fitzgerald, Solid State Commun. 11, 829 (1972).

12. G. Riblet and K. Winzer, Solid State Commun. 11, 175 (1972).
13. J. Takeuchi and Y. Masuda, J. Phys. Soc. Japan 44, 402 (1978).
14. P. Fulde and K. Maki, Phys. Rev. 141, 275 (1966).
15. P. Duwez, Progress in Solid State Chemistry (Pergamon Press, N.Y., 1966).
16. E. R. Domb, W. L. Johnson, J. Low Temp. Phys. 33, 29 (1978).
17. J. Kondo, Prog. Theor. Phys. 32, 1 (1964).
18. A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 39, 1781 (1960); Sov. Phys. JETP 12, 1243 (1961).