RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 5 1 MARCH 1985

Inhomogeneity-induced anomalous critical fields in metastable three-dimensional alloys

K. M. Wong and A. W. Clegg
Department of Physics, University of Virginia, Charlottesville, Virginia 22901

A. J. Drehman and S. J. Poon*
Ames Laboratory—U.S. Department of Energy, Iowa State University,
Ames, Iowa 50011

(Received 26 November 1984)

With low current densities (~ 2 A/cm^2), measurements of upper critical fields $H_{c2}(T)$ in amorphous thorium-based alloys exhibit narrow transitions ($\lesssim 3$ kG). The shape of $H_{c2}(T)$ deviates significantly above from the Maki curve (theoretical limit) and resembles those observed in some three-dimensional amorphous thin films. Increase in the current density by an order of magnitude, however, reveals increasingly broadened transitions (up to ~ 10 kG) and an additional transition but only at lower temperatures. Similar deviations, but to a lesser degree, are also observed in the coexistence region of the α and β phases in Hf and Zr alloys. Our results are explained in terms of inhomogeneous regions in metastable alloys. The present findings have important implications on the interpretation of superconducting properties in thin films.

Enhanced critical fields $H_{c2}(T)$ have been observed in several metastable bulk and thin-film superconductors.[1-3] The $H_{c2}(T)$ curves in these samples exhibit different degrees of deviation above the Maki curve and different transition widths. Several authors have attributed the anomalous behavior in $H_{c2}(T)$ to the effects of inhomogeneities in metastable alloys.[3-6] Recently, Zwicknagl and Wilkins[7] (ZW) put forth a thoery of inhomogeneous superconductors to explain both the deviation and increasingly broadening transitions with decreasing temperature. To cause large deviation of $H_{c2}(T)$ from the Maki curve, however, it would require very broad transitions according to the ZW theory. The transitions observed in some thin-film alloys, Mo-Re,[1] Mo-Si, and Mo-C,[2] showing almost linear $H_{c2}(T)$ curves, are narrow. Particularly, the transition widths in Mo-Re thin film (three dimensional) remain small (~ 2 kG) even in high fields. Apparently, this disagrees with the predictions of the inhomogeneity model.[7] On the other hand, enhanced critical fields are also predicted by the localization theory[8,9] which predicts reduced Coulomb repulsion in high fields. Therefore, from the physics standpoint, it is important to be able to differentiate these two effects. In this paper we report anomalous (almost linear) critical-field behavior in amorphous Th-based alloys (Th-Ni, Th-Co) observed at low current density. Increasing the current density manifests the inhomogeneity of the samples. Qualitative explanation of our results is given in terms of inhomogeneous regions in these materials. Results obtained in some crystalline Hf-based alloys are also used to address the inhomogeneity-localization problem in high-resistivity systems.

The Th-based alloy ribbons of compositions $Th_{75}Ni_{25}$, $Th_{70}Ni_{30}$, and $Th_{80}Co_{20}$ were prepared by melt spinning. Amorphicity was checked by x-ray diffraction. The $Hf_{87}Mo_{13}$ samples were produced by quenching onto a heated copper plate (180 °C) at a glancing angle in an argon atmosphere. Four terminal measurements down to ~ 0.5 K were performed in longitudinal fields. Details of experimental procedures have been provided previously.[10]

In Fig. 1, resistance as a function of applied magnetic field and current densities (2.2 and 32 A/cm^2) at different temperatures is shown for $Th_{75}Ni_{25}$. At low current density, the transition widths are defined by extrapolating the resistance-versus-field (R-H) traces along their steep slopes to 0% and 100% of the resistance. This results in rather sharp transitions ($\lesssim 3$ kG), comparable to those observed in homogeneous alloys.[10] The transitions are plotted as a function of temperature in Fig. 2. Apparent linearity is observed over an extended temperature range. Our results resemble those observed in three-dimensional (3D) amorphous Mo alloys.[1,2] The deviation from the Maki curve is significant, as can be seen in Fig. 2. Both dc resistance and ac susceptibility measurements also reveal sharp superconducting transitions. The former is ~ 20 mK and the latter is ~ 70 mK. Other Th alloys studied show similar properties. Thus, all evidences so far tend to suggest that the samples are homogeneous.

Apparently, the Th alloys, like the Mo alloys,[1,2] could be candidates for observing localization effects on $H_{c2}(T)$. On the other hand, the resistivity of these samples are rather low (~ 90–100 $\mu\Omega$ cm). Positive temperature coefficients of resistivity (TCR) are also observed, suggesting that local-

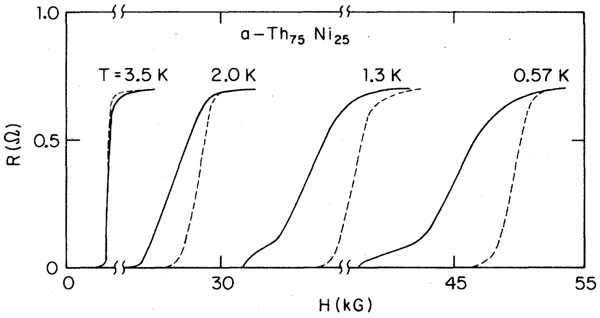

FIG. 1. Resistance vs field traces at several temperatures for amorphous $Th_{75}Ni_{25}$ sample. Dashed curves are taken at low current density (2.2 A/cm^2). Solid curves are taken at high current density (32 A/cm^2).

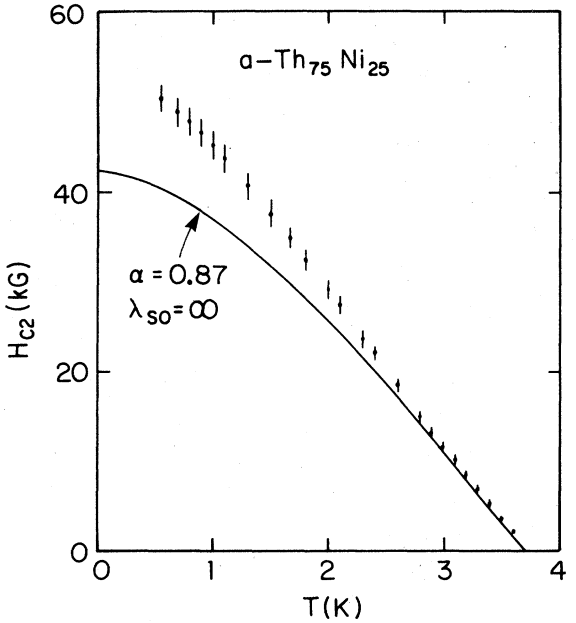

FIG. 2. Critical-field widths measured at low current density plotted as a function of temperature for $Th_{75}Ni_{25}$. Solid circles indicate midpoints of transitions. Solid line (Maki curve) is the WHH curve with spin-orbit parameter equals to infinity. The curve is a fit to the end points of the transitions.

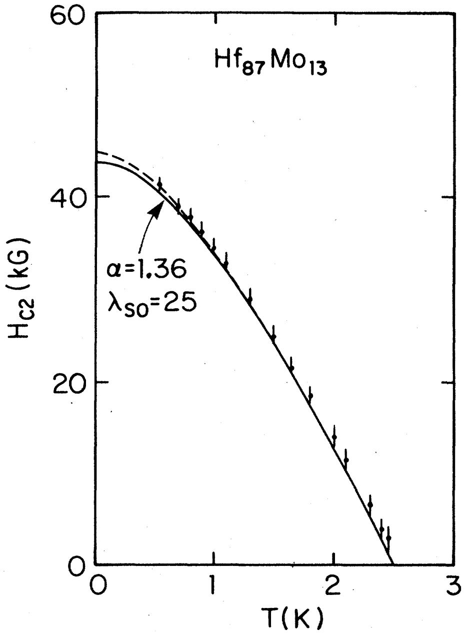

FIG. 3. Critical fields (including transition widths) as a function of temperature for crystalline $Hf_{87}Mo_{13}$ sample. Data were taken at a current density ~ 0.3 A cm^2. Solid line is a theoretical fit (WHH theory) to the extrapolated onsets of resistance. Dashed line is a fit to the Maki theory.

ization effects even if present, are very weak.[11] In view of this, we have also studied the $H_{c2}(T)$ behavior in stable crystalline (β phase) $Hf_{87}Mo_{13}$, alloys which have a negative TCR and typical resistivity values ($\sim 150\ \mu\Omega$ cm) observed in systems with weak localization.[12] The results are shown in Fig. 3. Data were taken at a current density ~ 0.3 A/cm^2. The extrapolated zero-resistance data points can be fitted to the Werthamer, Helfand, and Hohenberg (WHH) theory[13] with spin-orbit parameter $\lambda_{so} = 25$ and paramagnetic limiting parameter $\alpha = 1.36$ (see Ref. 10 for the least-squares-fitting procedure). This value of λ_{so} is in good agreement with results obtained from atomic calculation of Hf.[10] The negative deviation from the Maki curve (dashed line) is small but distinct. Increasing the current density did not broaden the transitions. We have also measured H_{c2} in Hf-Mo and Zr-Mo alloys at compositions near the β and α (or ω) phase boundary. These alloys contain traces of the α and ω phases with lower T_c values. Slight enhancement of H_{c2} above the theoretical curves for homogeneous alloys is noted.[10]

In view of the anomalous $H_{c2}(T)$ behavior and its possible correlation with inhomogeneity effects, we have measured $Th_{75}Ni_{25}$ samples obtained from three different quenches and $Th_{70}Ni_{30}$ from two different quenches. The results including the transition temperatures T_c are basically reproducible. We have also measured the $Th_{75}Ni_{25}$ samples after mechanically sanding off one-third of materials from either side of the ribbons. The results are similar to the virgin samples. This test is performed to check if there exists a distribution in crystallite inclusions across the thickness of the ribbon. A careful examination of the critical field curves in Th alloys, however, reveals slight positive curvatures in the temperature range 2–3 K. This fits the simple picture of the coexistence of two phases with T_c values ~ 3.4 and 3.7 K with different conductivities. Then, at low-current-density, percolation of the two superconducting phases throughout the entire sample is presumably complete.

One expects that a combination of high current density and high magnetic field would alter the percolation pattern as a result of inhomogeneity of the superconducting phases. The R-H traces at a current density ~ 32 A/cm^2 are illustrated in Fig. 1. Above 3 K, the transitions remain sharp. Near 2 K, the transitions have already broadened to ~ 5 kG. Below 2 K, a slight shoulder near the zero onset of the transition appears. At lower temperatures, this additional feature becomes more distinct. The shape of transition is reminescent of a two-phase material. The main transition responsible for most of the drop in resistance is broad. On the other hand, transitions in homogeneous samples (e.g., amorphous Zr-Rh alloys) remain sharp at the aforementioned current density.[10] In Fig. 4, we plot these transitions including the ones occurring in lower fields (closed circles). Treating our samples as two-phase materials, we have compared the lower critical transitions with WHH theory. The comparison is good and it is interesting to note that the values are comparable to those given by the solid line in Fig. 2 (data at low current density).

We associate the smeared transitions at higher fields with the phase having a slightly lower $T_c \sim 3.4$ K compared to 3.7 K. Since the two phases have rather similar electronic properties, it will be difficult to differentiate them from a structural point of view. Thus, it is also more appropriate to use the term regions rather than phases to describe them. We can only conjecture a certain topological structure to give a consistent account of our observations. It should be reminded that this is done only qualitatively. Suppose the high-T_c [low-$(dH_{c2}/dT)_{T_c}$] region is dominant in the samples. The low-T_c [high-$(dH_{c2}/dT)_{T_c}$] region percolates in

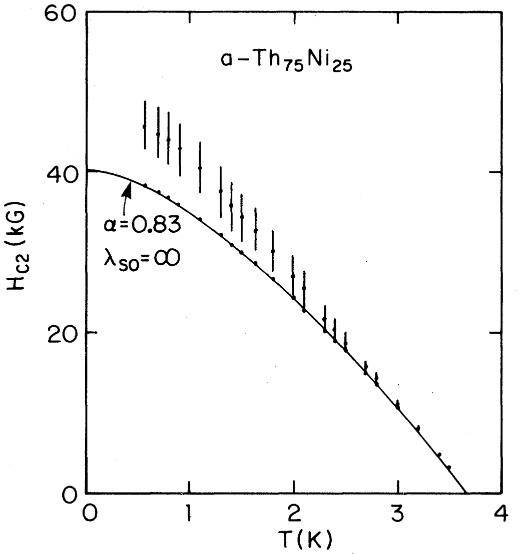

FIG. 4. Transition widths measured at high current density as a function of temperature for $Th_{75}Ni_{25}$. Solid line is a fit to the WHH theory. Solid circles along the theoretical curve are taken from the shoulders on the transition curves (see Fig. 1 and text).

the host via some "weakly connected" volumes. At low current density, the entire low-T_c region is fully connected. One then envisions a critical field curve as shown in Fig. 2. Increasing the current density at high fields destroys superconductivity along some of the "weak links" in the low-T_c region. This leaves the host (with slightly higher T_c) to form some of the connections. Then, one expects the appearance of finite resistance when the critical field of the host is reached provided H_{c2} (high T_c) $< H_{c2}$ (low T_c). The occurrence of shoulders (transition steps) at lower fields below ~ 2 K as shown in Figs. 1 and 4 is consistent with this picture. At increasing fields, superconductivity in the low-T_c region is gradually suppressed in the increasingly more connected volumes. As a result, the transitions are broadened. Low-field ac susceptibility measurement reveals only one transition around 3.7 K, suggesting that the majority phase "screens" the lower T_c minority phase.

The increasing broadening of transitions at decreasing temperature as shown in Fig. 4 is one of the features predicted by the Z-W theory for inhomogeneous superconductors.[7] However, this theory is not applicable in our Th alloys because the transitions remain sharp when the measurements are carried out at low current density. The scale of inhomogeneities in the present systems is probably more macroscopic than the ones proposed earlier.[4,7] It will be difficult to probe the structure of these inhomogeneities because they only have very subtle differences in their electronic properties. To investigate the correlation between the distribution of inhomogeneities and critical field behavior in the samples, additional experiments were performed. The freshly quenched Th-Ni samples were found to have different resistivity and TCR values from top to bottom of the ribbons, while T_c remained constant. Measurements were carried out after mechanically sanding the ribbons as discussed beforehand. Samples which were left at room temperature for three months did not show this sectional variation in transport properties. Thus, thermal relaxation at room temperature removed this "one-dimensional" distribution of the glassy states. For "easy glass formers" like $Zr_{75}Rh_{25}$ alloys, no such variation was detected. Critical fields and transition widths measured in the as-quenched, thermally relaxed (at room temperature), and sanded Th-Ni samples are almost identical.

For binary bulk alloys, our present results illustrate the first case of almost linearity in H_{c2} with sharp transitions over a wide temperature range. In bulk thin films of amorphous Mo alloys,[1,2] similar properties are obtained. It is conceivable that the anomalies observed in our alloys and thin films have a similar origin. As discussed beforehand, there is yet no evidence of weak localization effects on critical fields in bulk samples. The reason why weak localization effects are observed in magnetoresistance[12] but not in critical-field measurements will be discussed in a later publication. The degree of enhancement in critical fields seems to depend on the scale and type of inhomogeneities. Results obtained so far indicate that macroscopic crystallite inclusions having low-T_c values only produce small enhancements in critical fields. Examples are Hf-Mo, Zr-Mo,[10] Mo-Ru-B,[5] and Zr-Ni (Ref. 3) alloys in the mixed phases. To observe linearity in H_{c2}, it may require macroscopic "phase separation" into regions with almost the same properties in the samples. Our findings also imply that inhomogeneities can affect the electronic properties of thin films in a significant way.

The authors thank Dr. D. K. Finnemore for useful discussions. This work was supported by the Director of Energy Research, Office of Basic Energy Sciences, U.S. Department of Energy, through Contract No. WPAS-KC-02-01-01, and also by National Science Foundation Grant No. DMR-84-02624.

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[*] Permanent address: Department of Physics, University of Virginia, Charlottesville, VA 22901.

[1] M. Tenhover, W. L. Johnson, and C. C. Tsuei, Solid State Commun. **38**, 53 (1981).

[2] M. Ikeke, Y. Muto, S. Ikeda, H. Fujimori, and K. Suzuki, Physica **107B&C**, 387 (1981).

[3] S. J. Poon, S. K. Hasanain, and K. M. Wong, Phys. Lett. **93A**, 495 (1983).

[4] W. L. Carter, S. J. Poon, G. W. Hull, Jr., and T. H. Geballe, Solid State Commun. **39**, 41 (1981).

[5] B. M. Clemens, M. Tenhover, and W. L. Johnson, Physica **107B&C**, 319 (1981).

[6] S. J. Poon, Phys. Rev. B **25**, 1977 (1982).

[7] G. E. Zwichnagl and J. W. Wilkins, Phys. Rev. Lett. **53**, 1276 (1984).

[8] L. Coffey, K. A. Muttalib, and K. Levin, Phys. Rev. Lett. **52**, 783 (1984).

[9] H. Fukuyama, H. Ebisawa, and S. Maekawa, J. Phys. Soc. Jpn. **53**, 1919 (1984); also (unpublished).

[10] K. M. Wong, E. J. Cotts, and S. J. Poon, Phys. Rev. B **30**, 1253 (1984).

[11] R. W. Cochrane and J. O. Strom-Olsen, Phys. Rev. B **29**, 1088 (1984).

[12] S. J. Poon (unpublished).

[13] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966); H. Helfand and N. R. Werthamer, *ibid.* **147**, 288 (1966).