Anisotropy of H_{c2} in a cesium fluoroxide tungsten bronze*

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The T_c and H_{c2} of single crystals of nominal composition $Cs_{0.1}WO_{2.9}F_{0.1}$ were measured. The crystals studied grew in two forms, hexagonal needles and platelets. The Cs concentration, as measured by x-ray fluorescence analysis, was 0.1 ± 0.01 for the needles and 0.06 ± 0.006 for the platelets. T_c ranged from 4.87 to 4.94 K for both forms, with a transition width of 0.05 K. Upper critical field H_{c2} rotation data were taken using a standard four-lead contact method. H_{c2} data in the plane perpendicular to the crystal c axis showed an anisotropy having 60° periodicity, reflecting the hexagonal symmetry of the crystal. The anisotropy ratios ranged from 0.113 to 0.313 in this plane. Rotation in a plane containing the c axis showed 180° symmetry and anisotropy ratios ranging from 1.67 to 1.91, nearly as large as those found in layered structures. The temperature dependence of H_{c2} along three crystallographic axes is also reported.

There has been a great deal of recent interest in superconductivity in anisotropic compounds, particularly transition-metal dichalcogenides. In these materials, angular and temperature dependence of H_{c2} has shown anomalous characteristics.[1] We have measured H_{c2} in a material having a different crystallographic anisotropy and have made, we beleive, the first observation of hexagonal asymmetry in H_{c2}. The degree of anisotropy is one of the largest found outside of the layered structure compounds.

The material investigated was a hexagonal tungsten fluoroxide bronze with nominal composition $Cs_{0.1}WO_{2.9}F_{0.1}$. These compounds, of the general form $M_xWO_{3-x}F_x$, and their parent compounds the tungsten bronzes (M_xWO_3), vary in structure depending on type and concentration of the metal atom (M). The hexagonal structure, as shown in Fig. 1(b), is found to exist as a natural phase for M an alkali metal or an alkaline earth[2,3] when x is approximately in the range $0.2 \leq x \leq 0.33$. The M atoms are distributed along hexagonal channels surrounded by WO_6 octahedra, and are believed to contribute their valence electrons to the initially empty WO_3 conduction band. Typical unit-cell dimensions—within ~1% for all hexagonal bronzes—are $a = 7.4$ Å, $c = 7.6$ Å. The upper limit on x is dictated by stochiometric considerations, but the lower limit may be extended by substituting fluorine for some of the oxygen. This stabilizes the hexagonal structure and its metallic nature for x values at least as low as 0.05 and contributes an additional electron per F atom to the conduction band.[4] Such lower concentrations have been found to produce higher transition temperatures and critical fields.[5]

Romeika[6] *et al.* report an anisotropy of 0.5, $(H_{c\parallel} - H_{c\perp})/H_{c\perp}$, in the plane containing the c axis in acid-etched Rb_xWO_3, but no anisotropy in the plane perpendicular to the c axis. More recently Wanlass and Sienko[7] reported that no anisotropy was found in $Rb_{0.2}WO_3$.

Samples of hexagonal $Cs_{0.1}WO_{2.9}F_{0.1}$ (nominal) were prepared from high-purity CsF, W, and WO_3 by thermal vapor growth at 1050 C. The resulting

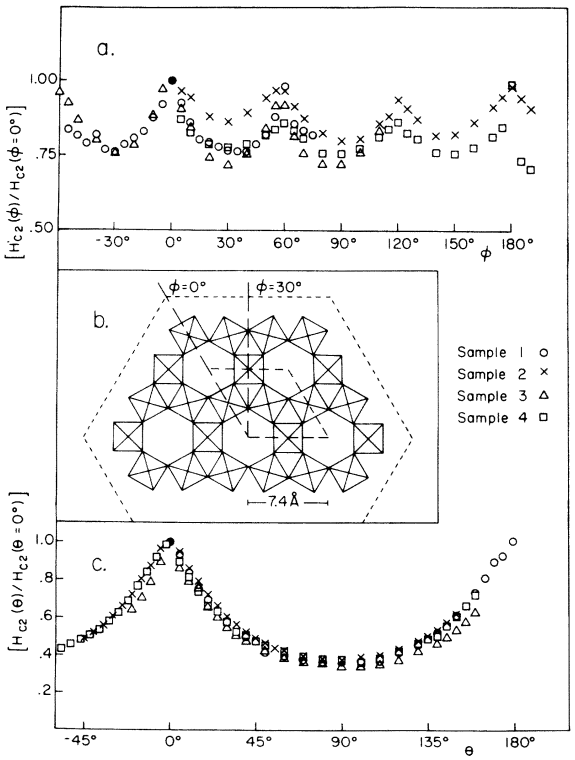

FIG. 1. (a) $H_{c2}(\phi)/H_{c2}(\phi=0)$ vs ϕ at 4.26 K: rotation in the plane perpendicular to the c axis. (b) 001 projection of hexagonal tungsten bronze structure defining the angle ϕ. External dotted lines show growth habit of hexagonal phase; internal dotted lines show unit-cell metal atoms lying along open hexagonal channels. (c) $H_{c2}(\theta)/H_{c2}(\theta=0)$ vs θ at 4.26 K: rotation in the plane containing the c axis.

crystals crystallized in three different habits: (i) filaments 3–5 mm in length and 5–10 μm wide; (ii) rectangular plates typically 4×4 mm×10 μm; (iii) crystalline and polycrystalline chunks typically 2 or 3 mm on a side. Optical and scanning electron microscope (SEM) examination revealed: (i) the filaments were of hexagonal cross section; (ii) the plates were planar, showed some evidence of filamentary structure, and cleaved most easily along the direction of the filaments; (iii) the chunks were partially formed hexagonal crystals. X-ray fluorescence measurements of the samples showed $x(\mathrm{Cs}) = 0.1 \pm 0.01$ and $x(\mathrm{Cs}) = 0.06 \pm 0.006$ for habits (i) and (ii), respectively. Sample forms (i) and (ii) gave essentially the same results, which is not surprising since it has been shown previously[5,7] that at low metal concentrations, T_c varies slowly with metal ion concentration. No information is available on the actual F content. The sharpness of the transition in our samples, typically 0.05 K wide ($\sim 0.01\ T_c$), implies good crystalline order. Room-temperature resistivity measurements indicate $\rho \approx 2.1 \times 10^{-4}\ \Omega$ cm. Ratios of resistance at 300–5 K ranged from 3.2 to 4.4 for the samples tested. The T_c values ranged from 4.87 to 4.94 K.

Several samples of forms (i) and (ii) were mounted on holders provided with four copper electrodes and electrical contact was made with silver paint. Standard four-lead electrical measurements were made for fields up to 12 kOe over a temperature range from 1.65 to 4.80 K. Temperature stability and measurement were within ±0.02 K. Bias currents were kept low enough, generally a few hundred microamperes, that the flux-flow phenomenom was negligible. In all cases the current flow was parallel to the filament axis, the c axis. We defined H_{c2} as the H intercept of the extrapolated linear portion of our resistance-versus-field curves.

Figure 1(a) shows $H_{c2}(\phi)/H_{c2}(\phi = 0)$ vs ϕ (rotation about c axis) at 4.26 K ($t \approx 0.87$). The angle ϕ is defined in Fig. 1(b). Values of $H_{c2}(\phi = 0°)$ ranged from 1.30 to 1.72 kOe for the samples measured. A marked anisotropy is observed with an angular periodicity of 60°. The magnitude of the anisotropy $[H_{c2}(0°) - H_{c2}(30°)]/H_{c2}(30°)$, averaged over several 60° intervals ranged from 0.113 to 0.313 for the various samples. An additional 180° over-all modulation in the data for the planar sample (4) seems to indicate an additional effect due to the planar geometry of the sample.

Figure 1(c) shows $H_{c2}(\theta)/H_{c2}(\theta = 0)$ vs θ (measured from the c axis) for $\phi \approx 30°$ at 4.26 K for the same samples as in Fig. 1(a). These $H_{c2}(\theta = 0°)$ values ranged from 2.89 to 3.61 kOe. The magnitude of the anisotropy, $[H_{c2}(0°) - H_{c2}(90°)]/H_{c2}(90°)$, ranged from 1.67 to 1.91.

Measurements of $H_{c2}(t)/H_{c2}(0)$ versus the reduced temperature, $t = T/T_c$, are shown in Fig. 2 for three sample orientations: (a) $\theta = 90°$, $\phi = 0°$; (b) $\theta = 90°$, $\phi = 30°$; (c) $\theta = 0°$. The data are normalized to the value of $H_{c2}(t = 0)$ predicted for each sample by Maki's theory of the temperature dependence of H_{c2}.[8] The theoretical curve was obtained by fitting the theory to the slope of the data at T_c. The average values of $(dH_{c2}/dT)_{T_c}$ for the orientations a, b, and c of Fig. 2 were made −2.32, −1.90, and −4.95 kOe/°K, respectively.

Comparison of Figs. 2(a) and 2(b) indicates that the magnitude of the anisotropy of H_{c2} in the ϕ plane is temperature independent, suggesting that the anisotropic behavior is due to the shape of the Fermi surface. The anisotropic effective mass model, a modification of the Ginzburg-Landau equation, does not agree with our observation since the effective mass tensor in the plane of sixfold symmetry is isotropic, thus predicting an isotropic H_{c2} in the ϕ plane.[9] For rotation in a plane containing the c axis [Fig. 1(c)] this model, while predicting an anisotropy, produces a relation which deviates considerably from the data. The effective-mass model does not describe this system. Several other theoretical attempts have been made to incorporate the effects of Fermi-surface anisotropy of H_{c2}, with only moderate success, and none of these attempts has considered the case of hexagonal symmetry. Additional theoretical work is clearly needed to produce a model for this system.

The data for $H_{c2}(\phi = 0°, t)/H_{c2}(0, 0)$ and $H_{c2}(\phi = 30°, t)/H_{c2}(0), 0)$ [Figs. 2(a) and 2(b)] in general fall above the theoretical predictions for isotropic type-II superconductors, which would result in a much higher $H_{c2}(0)$ than this theory predicts. In the case of sample 1, a positive curvature is observed. It has been suggested by Hohenberg and Werthamer that $H_{c2}(t = 0)$ will always be larger for materials with a nonspherical Fermi surface than would be theoretically predicted for a spher-

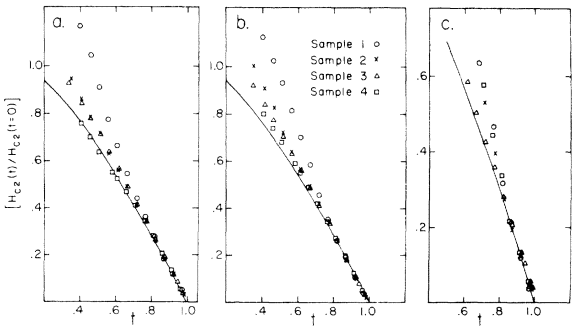

FIG. 2. $H_{c2}(t)/H_{c2}(0)$ vs t for three sample orientations (a) $\theta = 90°$, $\phi = 0°$; (b) $\theta = 90°$, $\phi = 30°$; (c) $\theta = 0°$ (parallel to c axis). The solid curve is the prediction of the Maki theory for isotropic type-II superconductors. The $H_{c2}(0)$ used for normalization was that predicted by this theory.

ical surface, but no estimate is given of the magnitude of this effect.[10]

As shown in Fig. 2(c), for H parallel to the c axis, the data again lie above the predictions of Maki's theory, and in addition show a positive curvature in $H_{c2}(t)/H_{c2}(0)$ vs t. Similar behavior in H_{c2} vs t has been observed in the layer structure compounds. Several theoretical attempts have been made to describe the behavior of the layered structures,[11] but it is not clear how any of these could be applied to the systems described here.

The data presented here clearly indicate that the tungsten fluoroxide bronzes, and most probably the tungsten bronzes, offer unique systems for the study of noncylindrically-symmetric anisotropy in both superconducting and normal properties. We are continuing our studies of the properties of these materials.

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