Conduction properties of the hexagonal tungsten bronze, Rb_xWO_3

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Studies of the electrical transport properties—resistivity, Hall effect, and Seebeck coefficient—of the hexagonal tungsten bronze Rb_xWO_3 for $0.16 \leq x \leq 0.33$ are reported for the temperature range from 1.5 to 300 K. In the normal state, these properties show temperature-dependent anomalies which suggest a phase transition with temperature. The temperature at which this transition occurs is shown to depend on the Rb concentration, exhibiting a sharp maximum near $x = 0.25$. As the Rb concentration is decreased below $x = 0.33$ the superconducting transition temperature first increases above the value of 1.94 K at $x = 0.33$ and then decreases to less than 1 K at $x = 0.24$. As the Rb concentration is lowered further a second increase in T_c is observed. This behavior appears to be associated with a phase transition at a composition near $x = 0.25$. The nature of neither the transition with temperature nor the transition with concentration could be precisely determined. The superconducting state shows a large temperature-independent 60° anisotropy in H_{c2} in the plane perpendicular to the hexagonal axis and positive curvature in the temperature dependence of H_{c2} near T_c.

I. INTRODUCTION

The electronic and structural properties of the *d*-band metals have received much recent attention.[1] One class of materials which fall within this broad classification is the tungsten bronzes, which are nonstoichiometric compounds of the general formula M_xWO_3 where M is one of a number of metal ions and x ranges from near 0 to 1. These materials crystallize in several different symmetries depending upon the size and valence of the ion M, and its concentration x.

The majority of the studies of the tungsten bronzes have centered on the cubic phase.[2] Of the elements for which this phase is possible, Na_xWO_3 has been studied in the most detail.

In this study, results are presented on the hexagonal tungsten bronze (HTB) Rb_xWO_3, which show it to have vastly different properties from those found in the cubic phase. In the hexagonal phase, WO_6 octahedra form 3- and 6-membered rings as shown in Fig. 1, leaving trigonal and hexagonal channels along the c axis. The radius of the hexagonal cavities is 2.00 Å, and will accomodate ions up to this size. These ions are believed to donate their valence electrons to the tungsten $5d(t_{2g})$ conduction band.[3] Many elements can be inserted into the hexagonal channels, although special techniques are required in some cases. The concentration range for which the hexagonal bronzes are believed to exist is $0.13 \leq x \leq 0.33$. The lower concentration has been estimated to be the thermodynamic phase limit[4]; however, in recent work Hussain was not able to produce hexagonal tungsten bronze (HTB) for $x < 0.19$.[5] The upper limit on x is set by complete filling of the hexagonal channels, and most previous studies of the hexagonal phase of Rb_xWO_3 have been at or near this upper limit.

The resistivity, ρ, of Rb_xWO_3 has been the subject of several investigations. Sienko and Morehouse[6] found a room-temperature resistivity of $(6.3 \pm 0.9) \times 10^{-5}$ ohm cm at $x = 0.33$ and an almost linear increase in ρ from 150 to 350 K. Sweedler[7] noted a linear rise in ρ above 50 K on a sample reported to be $Rb_{0.27}WO_3$. King *et al.*[8] have reported anisotropy in ρ for $Rb_{0.33}WO_3$, giving values at room temperature of 6.3×10^{-5} ohm cm along the c axis, and 3.6×10^{-4} ohm cm perpendicular to it. Their best samples gave linear ρ vs T behavior above about 40 K, with residual resistivity ratios (RRR) of ≈60.

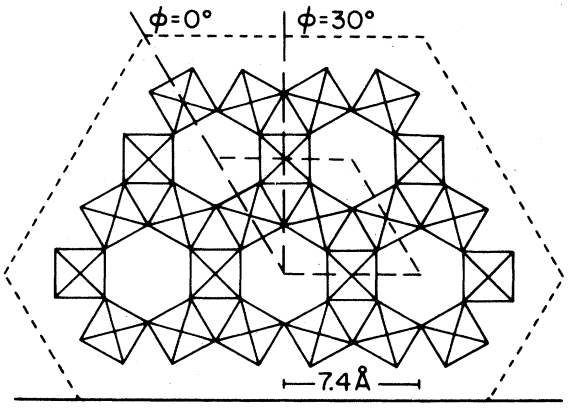

FIG. 1. Crystal structure of Rb_xWO_3 showing the projection in the plane perpendicular to the c axis. The squares represent WO_6 octahedra with the W atoms in the center. The Rb atoms reside in the hexagonal channels.

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Sweedler has observed a RRR of 236 on the samples described above and Stanley *et al.*[9] have found a RRR of about 4 for $Rb_{0.20}WO_3$.

The resistivity of another HTB, In_xWO_3, showed anomalous flattening in the c axis resistivity at about 215 K, and anisotropy of the a- and c-axis resistivities.[10]

The Hall coefficient of Na_xWO_3 (cubic and tetragonal phases) indicates that somewhat less than one electron is donated by the metal ion to the WO_6 conduction band with no variation of R_H with T in the region 1–300 K.[11] There are no reports of the Hall coefficient having been measured for any HTB.

Superconductivity was first observed in Rb_xWO_3 by Sweedler *et al.*[12] They observed $T_c = 2$ K and $\Delta T_c = 0.27$ K for $x > 0.3$ by ac susceptibility studies. Remeika *et al.*[13] found that T_c could be raised from 2.3 to values in excess of 7 K by acid leaching of some of the Rb. In contrast, Shanks and Danielson[14] have reported a linear decrease in T_c as x is lowered from 0.33 to 0.26. A completely different variation of T_c with x has been reported by Wanlass and Sienko.[15] They find that T_c rises from 2 K ($x = 0.33$) to 2.8 K ($x = 0.30$), and then falls sharply to below 1.2 K ($x = 0.28$). No superconductivity was reported above 1.2 K between $x = 0.28$ and $x = 0.24$, whereupon T_c rose rapidly to 4.3 K ($x = 0.20$).

The effect of a magnetic field on the superconducting properties of Rb_xWO_3 has been studied to some extent. Remeika *et al.*[13] have reported high values of H_{c2} in an etched sample at 4.2 K (x unknown). Wanlass and Sienko[15] have employed ac susceptibility techniques on crushed powder samples and show that the upper critical field increases as x is lowered. Single-crystal anisotropies in H_{c2} have been observed by Skokan *et al.*[16] in $Cs_{0.1}WO_{2.9}F_{0.1}$, which has the same structure as Rb_xWO_3. Similar anisotropies have been observed by Stanley *et al.* in $Rb_{0.20}WO_3$.[9]

Much lower critical fields have been observed by Bevolo *et al.*[17] at the filled limit, $x = 0.33$, and their observation of a latent heat in specific-heat measurements taken in a magnetic field led them to conclude that $Rb_{0.33}WO_3$ is a type-I superconductor.

The specific-heat measurements of Kienzle *et al.*,[18] King *et al.*,[8] and Bevolo *et al.*[17] have shown that $Rb_{0.33}WO_3$ obeys the simple relation $C = \gamma T + bT^3$ for the sum of the electronic and lattice components of the specific heat, between 2 and 3 K. At higher temperatures, an excess heat capacity is observed which they attributed to the presence of Einstein-like modes associated with the Rb ions. These investigators have obtained a Debye temperature of about 415 K, and an Einstein temperature, Θ_E, of 57 K for $Rb_{0.33}WO_3$ from their data. On etched samples, King *et al.*[8] have observed that Θ_E is about 67 K for $x \approx 0.2$.

Of the measurements outlined above, only those of Wanlass and Sienko[15] and Hussain[5] were taken on samples not grown electrolytically from Rb_2CO_3 and WO_3, or similar mixtures which will produce this HTB. Attempts to produce low-x HTB by etching these high-x samples has produced some confusion as to their x value, and to the homogeneity of the resulting crystals. Calorimetric measurements of T_c have given conflicting results.[8,17]

Some preliminary results on the work described in this paper have been reported previously.[19]

II. EXPERIMENTAL PROCEDURES

We have grown Rb_xWO_3 by solid-state reaction, and have been able to produce crystals with nominal x values as low as 0.16. $2\frac{1}{2}$ g of starting material were made up from high-purity Rb_2WO_4, W, and WO_3 and placed in quartz tubes which had been cleaned with hydrofluoric acid and distilled deionized water, and pumped to 10^{-7} Torr overnight at 1100 °C. The starting mixture was pumped for 13–18 h at $(2-8) \times 10^{-7}$ Torr before the tube was sealed. The mixtures were then heated at 950 °C for 5 days. The crystals which grew varied in appearance from long thin needles to short hexagonal prisms. Two batches at $x = 0.22$ and $x = 0.28$ were grown from Rb_2CO_3, WO_3, and W by first driving off the CO_2. As will be shown these samples had some different properties from those grown from Rb_2WO_4.

The Rb concentrations were checked by x-ray fluorescence analysis. The ratio of the counts in the Rb [$K\alpha$] to those in the W [$L\alpha$] peaks was found for each spectrum and compared with a calibration spectrum. Because of the failure to obtain a good calibration spectrum using mixtures of Rb_2WO_4 and WO_3, several small crystals of $Rb_{0.33}WO_3$ were run in a number of configurations and the Rb to W ratio of 0.33 was used as a standard. For each concentration a number of samples were measured and although there was some spread in measured x values, in all cases the nominal value was within the standard deviation (less than 5%) of the mean measured value. In the rest of this paper the nominal values will be used when denoting concentrations.

For resistivity measurements, samples were washed with acetone and weighed before being mounted for 4-lead measurements. All leads were attached with conducting silver paint, and when necessary currents up to 100 mA were passed through all the contacts to establish continuity. The cross-sectional area was calculated using the sample mass, length, and density. The density, calculated using the measured lattice parameters and the nominal Rb concentrations, obeys the linear relation, density $= 6.483 + 2.513x$ g/cm^3, to a linearity of better than 0.5% and an absolute accurate of about 1%. Resistive measurements were made in a helium-exchange gas system with current densities of typically 100 A/cm^2.

Hall-effect data was taken on several samples with current densities of several hundred A/cm^2 along the c axis, and a field of 11.5 kOe. Isenberg[20] geometry corrections were applied to those samples where accurate dimensions could be measured, but for several concentrations the inability to measure the sample geometry made the determination of absolute values of R_H impossible.

Seebeck-coefficient data has been taken for most concentrations from 90 to 300 K using copper-Constantan thermocouples for temperature measurement.

For the superconducting properties, we have measured T_c resistively using current densities of about 10 A/cm^2, and also inductively by the ac susceptibility method of Schawlaw and Devlin.[21] With a resonant frequency of 0.12 MHz, the skin depth of Rb_xWO_3 is about 0.9 mm, which is far larger than our samples.

The value of T_c for $Rb_{0.24}WO_3$ was determined by researchers at the Naval Research Laboratory[22] (NRL) and lattice-parameter measurements were made there as well as the University of California, San Diego.[23]

III. EXPERIMENTAL RESULTS

A. Normal-state properties

Lattice-parameter studies gave c and a axes which are in general agreement with reported values,[5] although those measured at NRL were smaller than those reported by other investigators. All samples measured were single phase. As the Rb concentration was decreased there was a decrease in line intensities and a broadening of the lines which would seem to indicate more disorder in the crystals; however relative line intensities were unchanged. Only normal Debye-Waller intensity increases were observed with decreasing temperature giving no indication of any temperature-dependent phase changes.[23] For $x=0.26$ one line showed an anomalous increase in intensity but its meaning could not be determined.

To check that the resistivity of $Rb_{0.33}WO_3$ grown by solid-state reaction (SSR) is similar to that of the same material grown electrolytically, we have measured 9 samples from T_c to 300 K. Typical temperature dependence of the resistivity of $Rb_{0.33}WO_3$ is shown in sample 33(12) in Fig. 2, with the average for the resistivity for all samples at 300 K being $(6.56 \pm 0.53) \times 10^{-5}$ ohm cm. This compares very favorably with the values of 6.3×10^{-5} ohm cm quoted by two other investigators.[6,8] Resistivity ratios of 20 to 30 were found for these samples, and the mean temperature coefficient of the resistivity at 300 K was 3.87×10^{-3} K^{-1}.

Figure 3(a) shows the resistivity at 4 K as a function of Rb concentration. The thermal contribution

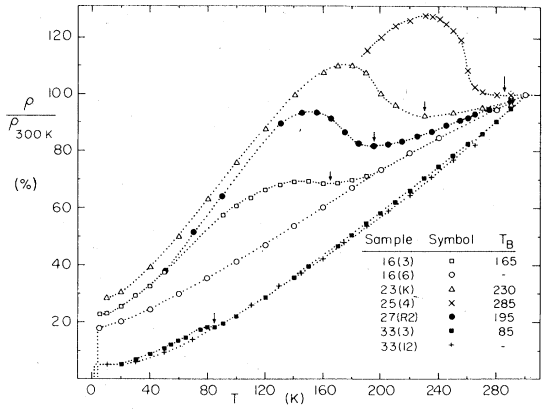

FIG. 2. Resistivity of Rb_xWO_3 as a function of temperature for various x values. T_B is the temperature at which the local minima in the resistivity occur.

to the resistivity at 300 K ($\rho_{300\,K}-\rho_{4\,K}$) is shown in Fig. 3(b). Except for the $Rb_{0.22}WO_3$, which was grown from carbonate material and the $Rb_{0.16}WO_3$, $\rho_{4\,K}$ rises monotonically but not linearly as x is decreased below 0.33. The value of $\rho_{300\,K}-\rho_{4\,K}$ for the carbonate grown $x=0.22$ is consistent with the other samples.

Figure 2 also indicates that at all concentrations below $x=0.33$, there is an anomalous hump in the resistivity. The temperature at which this anomaly

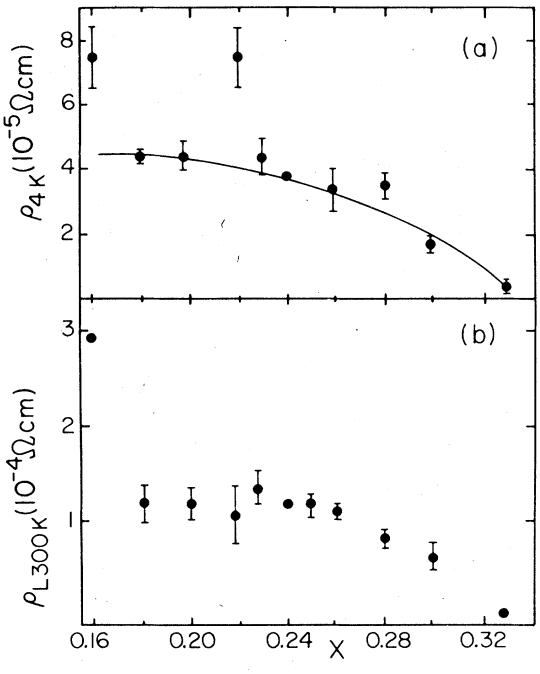

FIG. 3. Resistivity of Rb_xWO_3 as a function of x at 4 and 300 K. The solid state in (a) is a fit to the Nordheim relation for alloys, $\rho \propto x(0.33-x)$ at 4 K.

occurs, as well as its magnitude depends on the x value. The position of the minimum in the resistivity, T_B, is indicated by arrows for each concentration. The sample number gives the nominal Rb concentration. All the ρ vs T data were taken with current along the c axis except for the data on samples 16(6), which represents the resistivity in the a-b plane. The lack of any anomaly in this sample when compared to sample 16(3) in which the current is along the c axis would appear to indicate that the anomaly is unique to conduction along the c axis.

We have observed that the starting materials and residual resistance ratios do not seriously affect T_B. In Fig. 4, we present two plots for samples of $Rb_{0.28}WO_3$ grown from Rb_2WO_4 and Rb_2CO_3. The sample grown from Rb_2CO_3, 28(4), has a resistance ratio of 1.93, while that grown from Rb_2WO_4 has a higher resistance ratio of 3.27. Figure 4 indicates that while T_B is not seriously affected by the starting materials, the superconducting transition temperature T_c is.

The variation in T_B with x is shown in Fig. 5 where the error bars on the T_B axis represent the maximum spread of our data for all the samples which we have investigated. Such a spread in T_B could easily be accounted for by slight variations in the x values of the samples used. As can be seen, T_B shows a sharp peak at $x=0.25$. The anomalous hump in the resistivity is indicative of a phase transition with temperature for which the transition temperature is concentration dependent. However, x-ray diffraction measurements of lattice parameters above and below T_B show no change to within 0.0025 Å.[22,23]

Figure 6 shows the effect of the phase transition at T_B on the Hall and Seebeck coefficients. Good agreement exists at all concentrations between the temperatures at which slopes of the Hall and Seebeck plots change, and T_B of the resistivity plot.

The Hall coefficient at room temperature is $R_H=-(1.97\pm0.01)\times10^{-9}$ m^3/C, and use of

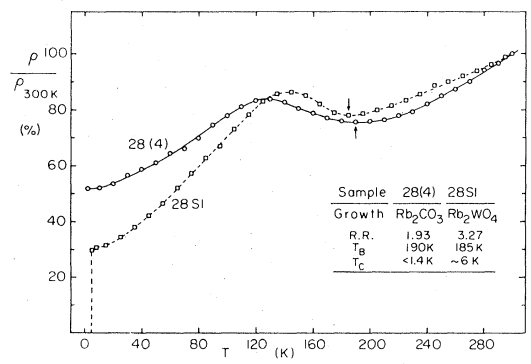

FIG. 4. Resistivity of $Rb_{0.28}WO_3$ as a function of temperature for crystals grown from rubidium carbonate and rubidium tungstate.

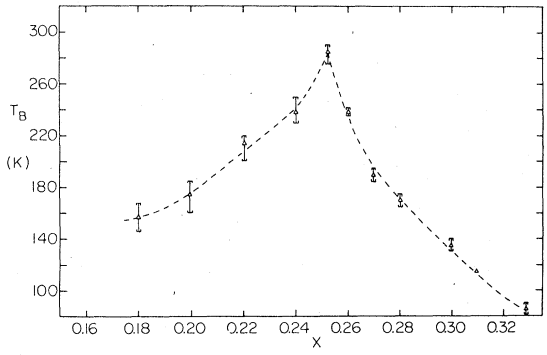

FIG. 5. Variation of the temperature T_B at which the high-temperature resistivity anomaly occurs for Rb_xWO_3 as a function of x.

$R_H=1/ne$ yields $n=(3.17\pm0.16)\times10^{27}$ electrons/m^3, or 1.12 ± 0.056 electrons/(unit cell). The size of the unit cell at this concentration is 3.5435×10^{-28} m^3. The $6x$ Rb atoms/(unit cell) with one electron per atom give a calculated value of electron concentration of 1.08 electrons/(unit cell), which is very close to our measured value, and consistent with the idea that the Rb atom donates its s electron to the WO_6 conduction band. Above T_B, R_H is essentially independent of temperature, but below T_B, R_H rises linearly, suggesting a change in the electronic character of the material at T_B and either a continuing decrease in electron concentration or mobility as the temperature falls.

The behavior of the Seebeck coefficient shown for $Rb_{0.18}WO_3$ in Fig. 6 is typical of all concentrations below $x=0.33$. Above the transition the coefficient is almost temperature independent while below the transition it decreases rapidly. At $x=0.33$, we have found that the Seebeck coefficient does not flatten

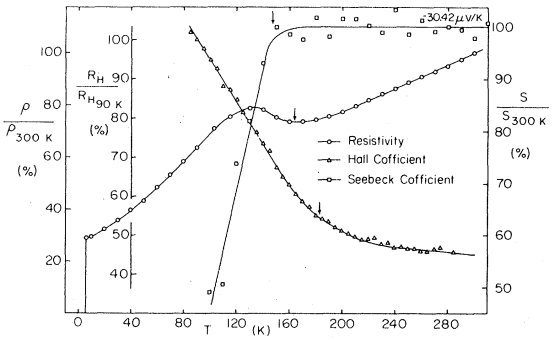

FIG. 6. Temperature dependence of resistivity, Hall coefficient, and Seebeck coefficient for $Rb_{0.18}WO_3$. This figure shows that the high-temperature anomaly is reflected in all three of these parameters. Behavior shown is typical for all Rb concentrations <0.33.

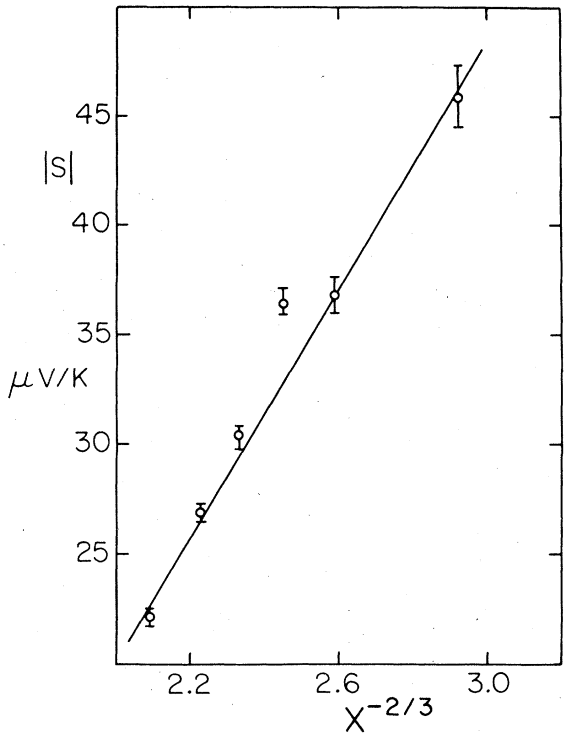

FIG. 7. Room-temperature Seebeck coefficient plotted against $x^{-2/3}$. This proportionality is the prediction of the free-electron model.

out at high temperature, as for all lower concentrations, but follows the linear relationship $-S = 4.55 + 5.84 \times 10^{-2} T\ \mu$V/K between 80 and 300 K, a temperature variation which seems more typical of a good metal, but with a relatively high room-temperature coefficient of about $-20 \pm 3\ \mu$V/K. As x decreases the coefficient at 300 K increases rapidly. The variation of S as a function of $x^{-2/3}$ is shown in Fig. 7. Error bars represent the standard deviation in the data, and the straight line is the best fit to five of the points. The simple free-electron theory predicts $S \propto n^{-2/3}$,[24] where n is the number of conduction electrons.

B. Superconducting properties

The results of our investigation of the variation of T_c with x on single-crystal samples is shown in Fig. 8, along with results from earlier investigations. In most cases, the T_c's were measured resistively. The inset table gives the transition widths, ΔT_c, defined as 10%–90% of the restored resistance. Transition widths quoted by Shanks and Danielson,[14] and by Wanlass and Sienko,[15] are given with their data points.

Our data suggest that superconductivity in Rb_xWO_3 is a very complicated phenomenon. At $x = 0.33$ all

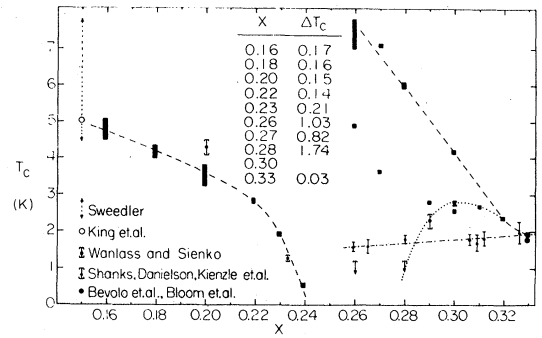

FIG. 8. Superconducting transition temperature T_c as a function of x for Rb_xWO_3. The solid squares and rectangles are present data and represent the spread in observed values. The dashed curve for $0.25 \leq x \leq 0.33$ corresponds to the maximum T_c observed in different crystals of a given composition. T_c's measured for the Rb_xWO_3 system by other investigators are also given.

samples had very narrow transitions widths and a T_c near 2 K which is in agreement with the values reported by all other investigators. For concentrations below $x = 0.33$ down to $x = 0.26$, the dependency of T_c on concentration is not clear. Samples of a given concentration in this range showed considerable variation in the T_c's. The dashed line for $x \geq 0.26$ represents the approximate maximum T_c's observed, but also as shown values considerably less than these maximum values were also seen. For example, for $x = 0.26$, some batches superconduct above 7 K, some at 5 K and some not above 1.5 K. Similar behavior is seen at $x = 0.27$. In this concentration range the transition widths also were considerably broader than at $x = 0.33$ or for $x < 0.25$. For $x \leq 0.25$, where transitions could be observed, they were relatively narrow and did not show the scatter exhibited at the higher concentrations. In this range the transition temperature again rises to a value in excess of 4.5 K at $x = 0.16$.

The scattered results for $0.26 \leq x < 0.33$ cannot be fully explained. T_c's measured using ac susceptibility were often less than those measured resistively which would seem to indicate the possibility of some type of surface superconductivity. Although we have not been able to answer this question, we find it strange that the maximum T_c's would scale with concentration the way that they are observed to do and also that this behavior is confined only to the region $0.26 \leq x < 0.33$.

In spite of these uncertainties, the drop in T_c near $x = 0.25$ and the subsequent increase again at lower concentrations coupled with the peak observed in T_B at this same concentration as shown in Fig. 5 are suggestive of a concentration-dependent phase transition.

We have also investigated the effect of Rb concentration on the c axis and basal plane anisotropies in H_{c2}. We find that anisotropies in both planes are

present throughout the entire range of x, although we were unable to obtain good absolute values for H_{c2} for those concentrations with wide superconducting transitions. Figure 9(a) shows the basal plane anisotropy of H_c for 2 samples of $Rb_{0.33}WO_3$ with the field normalized to $H_c(\phi = 60°)$. The table inset into Fig. 9 shows the reduced temperature at which the data was taken, and the values of the critical field at $\phi = 30°$ and 60°. The angle ϕ is defined in Fig. 1. These critical fields are the smallest that we have observed in the Rb_xWO_3 system. Since the critical fields are small and Bevolo *et al.*[17] suggests that $Rb_{0.33}WO_3$ is a type-I superconductor, the critical-field data at the orientations $\phi = 60°$ and 30° in Fig. 9(b) were fit to the prediction of the BCS theory by matching the slopes, dH_c/dT, at $t = 1$. The slopes at $t = 1$, the critical fields at $t = 0.8$, and the anisotropy A, which we have defined as

$$A = \left[\frac{H_c(60°) - H_c(30°)}{H_c(60°) + H_c(30°)}\right]_{t=0.8}$$

are given for $x = 0.33$ and other concentrations in Table I. For the $x = 0.33$ samples, excellent agreement is observed between the field parameters at $\phi = 30°$. The values at $\phi = 60°$ are larger in all cases but show considerable variation. The slope of the critical field versus temperature at T_c for $Rb_{0.33}WO_3$ has also been measured by Bevolo *et al.*,[17] although the orientation of their sample to the field was un-

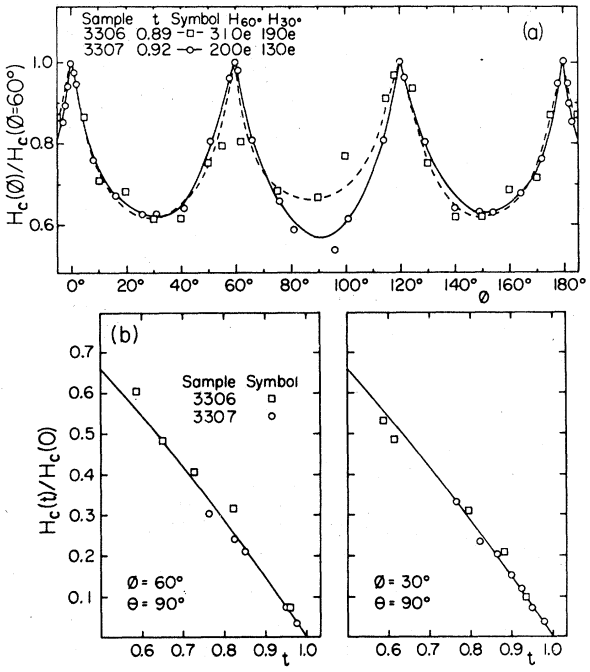

FIG. 9. (a) Anisotropy of H_{c2} data for $Rb_{0.33}WO_3$ as a function of angle (ϕ is defined in Fig. 1) of the applied field in the plane perpendicular to the c axis showing the 60° anisotropy. (b) The reduced field vs reduced temperature at the maxima and minima of H_{c2}. The solid lines are the fit of the data to the BCS theory.

TABLE I. Superconducting transition temperatures and critical-field parameters for fields in the hexagonal plane for Rb_xWO_3 where the sample number equals x times 100. ϕ is defined in Fig. 1 and A is defined in the text.

		$\phi = 60°$			$\phi = 30°$			
Sample number	T_c (K)	$-dH/dT$ (kOe/K)	$H(0)$ (kOe)	$H(t=0.8)$ (kOe)	$-dH/dT$ (kOe/K)	$H(0)$ (kOe)	$H(t=0.8)$ (kOe)	A
18(1)	4.15	4.72	13.4	8.70	3.86	10.90	3.40	0.44
18(2)	4.10	4.40	12.3	6.85	3.40	9.56	3.55	0.32
18(3)	4.28	6.70	19.3		5.10	14.8	4.34	0.45
18(6)	4.20	6.30	17.9	7.80	3.20	9.4	3.30	0.40
20(1)	3.52	7.20	17.4	4.57	2.87	6.8	1.90	0.41
20(2)	3.55	1.93	4.7	1.50	5.51	3.6	1.10	0.15
20(3)	3.73	6.83	17.4	5.40	3.56	9.1	2.60	0.35
20(4)	3.26	5.03	11.1	3.26	2.10	4.7	1.65	0.33
20(5)	3.88	7.14	18.8	5.45	2.80	7.7	2.3	0.38
20(6)	3.59	5.62	13.8	3.66	3.16	7.8	2.10	0.27
20($R2$)	3.20	3.97	8.7	2.50	2.05	4.5	1.52	0.24
22($R1$)	2.90	1.06	2.11	0.61	1.03	2.06	0.57	0.03
22(2)	2.80	0.86	1.57	0.49	0.76	1.38	0.45	0.05
32(3)	2.37	0.256	0.42	0.11	0.22	0.36	0.09	0.10
33(6)	1.93	0.155	0.140	0.052	0.092	0.082	0.037	0.17
33(7)	1.94	0.129	0.177	0.046	0.087	0.079	0.037	0.11

known. Our value of dH/dT at T_c for $\phi = 30°$ is in excellent agreement with the value of 94 ± 5 Oe/K quoted by them. Our values of $H(0)$ are much lower than the 645 Oe found by Wanlass and Sienko.[15]

Anisotropy in H_{c2} has been the subject of many recent investigations,[25] but the HTB show the first 60° anisotropy of H_{c2} in an hexagonal metal. Kostorz *et al.*[26] have searched for anisotropy in H_{c2} in the hcp metal ^{99}Tc, but found none.

In Fig. 10 is shown critical-field rotation data which is typical for all concentrations below $x = 0.33$. Field parameters for a number of concentrations are given in Table I. The enhanced values of H_{c2} found at $\phi = 0°$ and 180° were observed in a number of samples and may be due to the planar shape of the samples.

The larger values of H_{c2} below $x = 0.33$ indicate that the materials are probably type-II superconductors; thus we have estimated $H_{c2}(0)$ by fitting the slope of our data at $t = 1$ to the Maki theory for dirty type-II superconductors.[27] As illustrated in Fig. 10 there is an upward positive curvature in much of our critical field versus temperature data near $t = 1$, which may in many cases render our estimates of $H_{c2}(0)$ too low. This curvature is generally not observed below $t = 0.8$.

An examination of the Table I yields a number of interesting facts. When the concentration is decreased to 0.32, all the field parameters increase from $x = 0.33$ values. Our estimates of $H_{c2}(0)$ are 415 Oe at $\phi = 60°$ and 358 Oe at $\phi = 30°$, which are again lower than the value of 925 Oe quoted by Wanlass and Sienko.[15]

When the concentration is decreased to the region below $x = 0.24$ the critical-field parameters increase significantly giving $H_{c2}(0)$ values as high as 14 kOe. We have measured field data on samples grown by SSR from both Rb_2WO_4 and Rb_2CO_3. The samples 22(R1) and 22(2) are from a batch of $Rb_{0.22}WO_3$ grown from Rb_2CO_3. As shown in Table I, the anisotropy is depressed in these samples as compared to samples grown from the Rb_2WO_3. Field rotation plots and field dependence fits for $Rb_{0.20}WO_3$ were presented in our earlier report.[9]

Measurements of the critical fields for fields in the plane of the c axis are given in Table II and typical behavior is illustrated in Fig. 11. Extrapolated value at the zero-resistance baseline of the tangent through the point of inflection in the restored resistance versus applied field curves was taken as the value of H_{c2}. These values represent a lower limit of H_{c2}. For $Rb_{0.33}WO_3$, the slope, $-dH/dT$, at T_c for sample 33(6) at $\theta = 0$ is 320 Oe/K which is considerably larger than the values for $\theta = 90°$ at $\phi = 30°$ and 60°. The BCS estimate of $H_c(0)$ is 297 Oe, and the aniso-

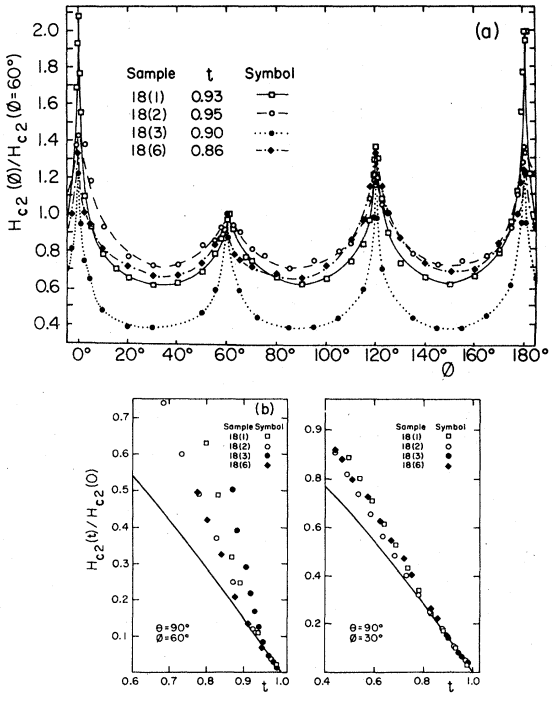

FIG. 10. (a) Anisotropy of H_{c2} in the plane perpendicular to the c axis (ϕ is defined in Fig. 1) showing the large hexagonal anisotropy for $Rb_{0.18}WO_3$. (b) The variation of the reduced field with reduced temperature. The solid lines represent fits to the Maki theory (Ref. 25).

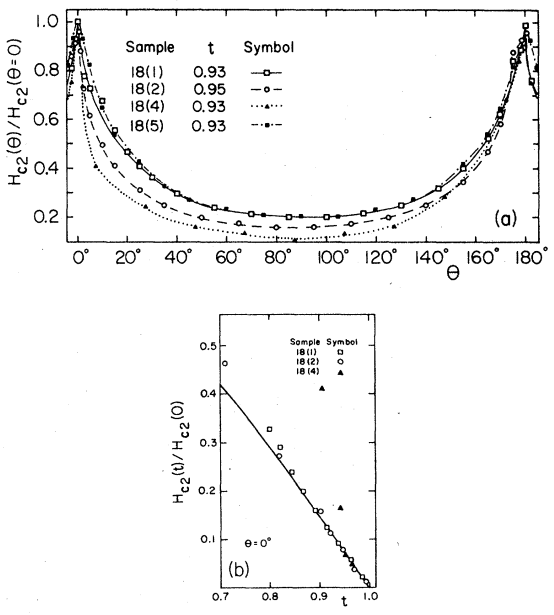

FIG. 11. (a) Anisotropy of H_{c2} in the plane containing the c axis with ϕ near 30° (ϕ is defined in Fig. 1) and $\theta = 0$ is along the c axis. (b) The reduced field vs the reduced temperature. The solid curve is a fit to the Maki theory (Ref. 25).

TABLE II. Superconducting transition temperature and critical-field parameters for fields in the plane of the c axis for Rb_xWO_3 where the simple number equal x times 100. $\theta = 0°$ corresponds to a field along the c axis. A' is defined in the text.

		$\theta = 0°$			$\theta = 90°$			
Sample Number	T_c (K)	$-dH/dT$ (kOe/K)	$H(0)$ (kOe)	$H(t=0.8)$ (kOe)	$-dH/dT$ (kOe/K)	$H(0)$ (kOe)	$H(t=0.8)$ (kOe)	A'
33(06)	1.98	0.32	0.297	0.099				0.49 ($t=0.73$)
33(12)	1.96							0.47 ($t=0.86$)
22(1)	2.85	1.53	3.82	1.13				0.06 ($t=0.65$)
22(7)	3.86	1.22	3.17	0.90				0.64 ($t=0.73$)
20(1)	3.52	20.3	48.6	14.3 (ex)[a]	3.33	8.00	2.30	0.73 ($t=0.90$)
20(4)	3.27	13.9	31.7	9.8				0.75 ($t=0.90$)
20(6)	4.16	16.9	47.7	14.0 (ex)	3.22	9.10	2.60	0.68 ($t=0.87$)
18(1)	4.26	10.6	30.8	10.2				0.66 ($t=0.93$)
18(4)	4.00	6.1		20.8 (ex)				0.81 ($t=0.93$)
18(5)	4.24				4.71	13.64	4.00	0.67 ($t=0.93$)

[a]Values identified with (ex) were estimated as expiained in the text.

tropies, A', for the two $Rb_{0.33}WO_3$ samples calculated from,

$$A' = \frac{H_c(0°) - H_c(90°)}{H_c(0°) + H_c(90°)}$$

were 0.49 and 0.47. As in the case of the ϕ variation, this anisotropy was found to be essentially temperature independent.

The difference between samples of $Rb_{0.22}WO_3$ grown from Rb_2CO_3 and Rb_2WO_4 is again seen in Table II. For sample 22(1), made from Rb_2CO_3, the anisotropy is much less than that of sample 22(7), made from Rb_2WO_4 in agreement with what was observed in the hexagonal plane.

Since our field measurements were limited to 12 kOe in these experiments, we have had to estimate three values of $H(t=0.8)$ for samples 20(1), 20(6), and 18(4) (see Fig. 11), and these are denoted by (ex) in Table II. The large amount of positive curvature for sample 18(4) makes it impossible to estimate $H_{c2}(0)$ for this sample.

IV. DISCUSSION

The basic resistivity mechanisms in the HTB have not previously been thoroughly investigated. $Rb_{0.33}WO_3$ shows no indication of the anomalous hump in the temperature dependence of the resisitivity found at lower concentrations and thus its behavior is taken to reflect the basic conduction properties of the HTB. Above 100 K the resistivity rises in an essentially linear manner with temperature. This can be compared to the cubic system Na_xWO_3 where $d\rho/dT$ increases continuously up to 870 K. However, the electron mobility at 300 K in $Rb_{0.33}WO_3$, calculated assuming one electron per Rb atom, which the Hall data appears to justify, is 17.0 cm^2/V sec. This is the same order of magnitude as the mobility found in the Na system and suggests a common transport mechanism for all the tungsten bronzes. Sienko and Morehouse[6] attempted to attribute the temperature dependence of the resistivity in $Rb_{0.33}WO_3$ to the polar scattering of conduction electrons from optical phonons, a model which had been successful in explaining the behavior in WO_3, an n-type semiconductor. In the region above 150 K, their model appears to give a good fit to the data but it fails to explain the large temperature variation of ρ at low temperatures found in this work, which shows an approximate T^3 dependence below 50 K (two samples gave exponents of 2.81 and 2.91, respectively).

King *et al.*[8] measured a Debye temperature in $Rb_{0.33}WO_3$ at 415 K. However the concept of a Debye temperature for the HTB is complicated by the crystal structure which allows for the vibration of the Rb ions within the channels in the host lattice of WO_6 octahedra. Heat-capacity studies suggest the Rb ions vibrate in Einstein-like modes with a characteristic temperature of 57 K. Inelastic neutron scattering studies have recently confirmed the existence of such Einstein-like modes.[28] For a Debye temperature above 400 K, the lattice contribution to the resistivity should show a continually increasing contribution with temperature in the region investigated, as is the case in Na_xWO_3. However, a large contribution from the scattering due to Einstein modes with $\Theta_E = 57$ K could result in a linear increase in resistivity at high temperatures since $\rho \propto T/\Theta_E$ above Θ_E. The approximate T^3 dependence of ρ at low temperatures is also not inconsistent with scattering predominantly from the Einstein-like modes of the Rb ions, especially in view of the relatively large scatter in the data.

The residual resistance, $\rho_{4\,K}$, shown in Fig. 3(a) indicates that Rb ion vacancies are significant in the residual scattering. As shown in the figure, over the range of concentrations investigated, the resistivity follows the Nordheim relation[29] for the resistivity of alloys, i.e.,

$$\rho_{4\,K} \propto x(0.33 - x) \ ,$$

where the Rb ions and the vacancies play the role of the alloy constituents.

Any consideration of the phase change at concentrations below $x = 0.33$ has been neglected in this fitting and it seems somewhat strange that the residual resistance in $Rb_{0.33}WO_3$, which does not show the transition, should be in agreement with the lower concentrations which do show a transition. The most significant difference seems to show up in the residual resistance ratios, where $Rb_{0.33}WO_3$ had ratios as high as 30 whereas for concentrations $x = 0.30$ and below, RRR's were around 3–4. The high value of the residual resistivity in the carbonate grown $Rb_{0.22}WO_3$ sample would indicate a significant increase in the impurities in this material. The room-temperature lattice resistivity, however, is consistent with noncarbonate grown crystals indicating that the impurities do not appreciably affect the temperature-dependent resistivity. The high-resistivity value for the $x = 0.16$ sample probably reflects a significant increase in lattice distortion as the phase limit is approached or possibly the phase separation of the nominal $x = 0.16$ into a mixture of Rb_xWO_3 with $x > 0.16$ and WO_3 as has been previous observed.[5] X-ray diffraction studies were not done on this concentration, thus the question cannot be answered for certain.

At all concentrations below $x = 0.33$, a hump appears in the resistivity, the position and magnitude of which depend strongly on the concentration. Corresponding anomalies which also appear in the Hall and Seebeck coefficient confirm the occurence of what is probably some type of phase transition. However, x-ray diffraction studies show no structural transition to within the accuracy of the measurements, 0.0025 Å.[22,23] Resistance anomalies have been observed in the HTB In_xWO_3,[10] and in cubic Li_xWO_3,[24] but no mechanism for the anomalies has been suggested. In the *d*-band metals, resistive anomalies associated with phase transitions commonly occur, in particular with martensitic transitions. Very small structural phase transitions with temperature have recently been observed in cubic Na_xWO_3 but these transitions do not produce observable changes in the electrical properties.[30]

Recent theory has indicated that *d*-band metals with relatively large density of states at the Fermi surface possess a tendency toward collective electron instability which is characterized by a periodic charge redistribution.[31] These charge fluctuations are strongly coupled to the lattice and create anomalies in the phonon spectra, structural transitions, or possibly a charge-density wave (CDW). The former two of these possibilities have both been observed to occur in the cubic tungsten bronze, Na_xWO_3.[32,33] In Rb_xWO_3 the possibility of a lattice distortion which is too small to be detected in the x-ray diffraction measurements which have been made to date cannot be ruled out. Neither can the possibility of the formation of a CDW be ruled out. The anomaly in the temperature dependence of the resistivity would certainly be explained if such a transition occurs. Also the energy gaps which open up with CDW formation could result in a Hall coefficient which rises with decreasing temperature below the transition as is observed for Rb_xWO_3 as shown in Fig. 6. The cubic phase shows no such variation in R_H which remains constant from 1 to 300 K.[11]

However, it is difficult to see how to explain the concentration dependence of the transition shown in Fig. 5 within this model. If vacancies in the Rb lattice act as scattering centers as the resistivity data seems to indicate, then it would be reasonable to assume that they would also tend to drive the phase-transition temperature down since impurities are in general destructive to CDW formation. As Fig. 5 shows, this is not the case. The transition temperature increases with decreasing concentration to a sharp maximum at $x = 0.25$ and then decreases. It is interesting to speculate that there is a form of ordering of the Rb atoms near $x = 0.25$ which could be commensurate with a possible CDW and thus assists the formation of the CDW. While there is no evidence for ordering in Rb_xWO_3 (the line intensity would be expected to be only about 1% of the strong W lines and thus too weak to be observed in the x-ray diffraction experiments); evidence of ordering has been observed in cubic Na_xWO_3 near $x = 0.75$.[34]

Other than the peak observed in the transition temperature T_B at $x = 0.25$, no other changes in the electrical properties were seen as x is lowered through $x = 0.25$. This would seem to indicate no major changes in the Fermi-surface geometry. Measurement of the room-temperature Seebeck coefficient, S, support this contention. As mentioned before, simple free-electron theory predicts that $S \propto n^{-2/3}$ where n is the number of conduction electrons. Figure 7 shows that the room-temperature Seebeck coefficient increases as $x^{-2/3}$ indicating a consistent depopulation of the conduction band as the Rb concentration is decreased.

While the absolute values of S are similar to those of other tungsten bronzes the variation of S with temperature is difficult to explain. The reason for the almost temperature-independent behavior of S above T_B is not clear since in the free-electron model $S \propto T$ and this is observed for $x = 0.33$. Hopping models of electrical conductivity have been used to

explain Seebeck coefficients which are temperature independent at high temperature in pseudo-one-dimensional systems,[35] but there is no evidence for the localization of electrons in Rb_xWO_3 which this model would require. For $x=0.33$ an effective mass can be calculated in the almost free-electron picture since

$$S=\tfrac{2}{3}(\tfrac{1}{3}\pi)^{2/3}(\alpha k_B 2/e\hbar^2)\,Tn^{-2/3}\ ,$$

where $\alpha=m^*/m_0$. Taking one electron per Rb ion or $n=x$, we get $\alpha=2.75$ which is very close to the calorimetrically determined value of King *et al.*[8]

Concentration-dependent phase transitions have been observed in cubic tungsten bronzes. At $x=0.25$ Li_xWO_3 undergoes a metal-insulator transition,[24] while Na_xWO_3 shows several structural transitions with concentration with all phases being metallic.[30] However, no transitions have previously been observed in HTB.

The effect of the phase transition at $x=0.25$ can also be seen in the superconducting transition temperature which shows a pronounced minimum for a Rb concentration near $x=0.25$ as seen in Fig. 8. Above this critical concentration the measured T_c's show varied behavior as has been previously described making it very difficult to speculate on the factors affecting T_c.

In the cubic Na_xWO_3 system, the superconducting transition temperature increases almost exponentially from about 0.75 K at $x=0.40$ to about 3 K at $x=0.20$[33] as the concentration approaches the phase transition from tetragonal I to tetragonal II which occurs at $x=0.2$. Several theories have attempted to explain this increase based primarily on a decrease in lattice stability which results in a softening of the phonon modes and an enhanced electron-phonon interaction and thus an increase in T_c.[36] As the phase boundary is approached the increasing instability in the lattice results in high T_c's up to some maximum where the distortion of either the lattice or electron coordinates stabilizes the low-concentration phase with a consequent drastic reduction in T_c. The high T_c's observed for $x\geq 0.26$ could result from a similar mechanism, although the nature of the phase below $x=0.26$ which would bring on a lattice softening is not clear.

However, the high T_c's did not prove to be very reproducible and could result from some type of surface effect in our crystals. It may well be that the T_c's of the bulk material show first an increase down to near $x=0.28$ and then a decrease below this concentration similar to the data of Wanless and Sienko.[15] In spite of this uncertainty the one thing that is clear is that around $x=0.25$ some type of transition in behavior is occurring.

The increase in T_c at 5 K at $x=0.16$ as the concentration is decreased below $x=0.25$ also remains unexplained. One could invoke the argument above that another phase of instability is being approached at low concentration, which as we have mentioned is true; however, it is certainly not clear why T_c should increase so rapidly below $x=0.25$ or in fact why this particular phase should be superconducting at all. Examination of the data would seem to indicate that around $x=0.25$ there exists a particular phase or "pseudophase" which is not conducive to superconductivity. The nature of this pseudophase and whether it could be tied to some ordering of the Rb ion is unknown. It is interesting to note that in the HTB, Cs_xWO_3, with its larger and heavier Cs ions, no such anomaly in T_c is observed[37]; however, for the lighter K ions there is some preliminary evidence of a similar anomaly.[38] The model of the superconducting state based on the Einstein modes associated with the motion of the alkali ions in the WO_3 lattice, which seemed to possibly explain the variations in T_c with different alkali ions in the HTB for $x=0.33$,[17] fails completely to explain the variations in T_c for $x<0.33$ since it predicts a decreasing T_c with decreasing x below $x=0.33$.

Another property of the superconducting state in Rb_xWO_3 is the large hexagonal anisotropy in H_{c2} about the c axis. This anisotropy exists throughout the concentration range $0.18\leq x\leq 0.33$, increasing in value as x decreases. In addition there is also a twofold anisotropy in H_{c2} in the plane of c axis. In this plane one could certainly use some type of effective-mass model,[39] as has been done extensively in the layer-structure materials, to describe the behavior to at least some approximation, but such a model predicts isotropic behavior in the hexagonal plane, completely contrary to the data. One is then forced to look at a more detailed model based on an anisotropy of the Fermi surface, phonon spectrum, or electron-phonon coupling, or some combination of these. Several such theories exist,[40] but in all cases they predict an anisotropy which is small and temperature dependent. This however is not the case for the Rb_xWO_3 system and further theoretical work on anisotropic superconductors will be necessary to explain these experimental results.

The magnitude of H_{c2} as a function of Rb concentration and temperature also shows interesting properties. As Table I shows, the critical fields of $Rb_{0.33}WO_3$ are very low when compared to the values of H_{c2} observed at lower concentrations. These low values are in essential agreement with the value quoted by Bevolo,[17] who concluded, based on the low value of H_{c2} and heat-capacity data, that the stoichiometric compound was in fact a type-I superconductor. It is interesting that the decreasing Rb concentration decreases the critical field so dramatically and that the hexagonal anisotropy in the critical field at $x=0.33$ is large ($A\approx 0.15$) even though the fields are small.

Our attempts to fit the temperature dependence of the critical-field data to the Maki theory for dirty type-II superconductor[27] in many cases have displayed significant disagreement at low temperatures due mainly to the positive-upward curvature near $t=0$ in low-x samples. Such positive curvature has been observed in other highly anisotropy materials, such as the layer-structured materials.[41] A recent theory[42] using an effective two-band model has attempted to explain similar behavior of H_{c2} in the compound $Cs_{0.1}WO_{2.0}F_{0.1}$,[16] which has a similar structure to Rb_xWO_3 and a reasonable fit to the positive curvature in H_{c2} versus temperature data was obtained. Assuming no electron-phonon coupling between the bands and no interband scattering by impurities, the H_{c2} vs T curves can be constructed from a mixture of contributions from the bands. Because of the similarity in structure of the compounds, this theory should apply to the Rb_xWO_3 systems; however the details are certainly not clear.

V. CONCLUSIONS

At room temperature and below all the current data on $Rb_{0.33}WO_3$ is consistent with a conduction mechanism which consists predominantly of electron scattering from the Einstein-like modes associated with the Rb ions. For concentrations below 0.33, however, temperature-dependent anomalies in the electrical transport properties occur which strongly suggest some type of temperature-dependent phase transition. While the exact nature of this transition could not be determined, the lack of an observable change in the crystal structure as a function of temperature, coupled with large changes in the electrical properties with temperature seems to indicate something more than a simple crystal structure transformation. Furthermore, the concentration dependence of this phase transition exhibits a sharp maximum in the phase-transition temperature T_B, near $x=0.25$. This maximum in T_B coupled with an anomalous drop in T_c near $x=0.25$ seems to indicate a phase transformation at a composition near $x=0.25$, the nature of which is currently indeterminant. The difference between the concentration dependence above and below $x=0.25$ of the temperature T_B at which the resistive anomaly occurs indicates a correlation between the composition and the temperature-dependent phase transitions.

The superconducting state in Rb_xWO_3 shows a large temperature-independent 60° anisotropy in H_{c2} in the plane perpendicular to the c axis which appears to not be explainable in the context of current theories of anisotropic superconductors. The temperature dependence of H_{c2} shows a positive curvature near T_c which has been previously observed in many highly anisotropic materials.

Rb_xWO_3, and in general the hexagonal M_xWO_3 compounds, appear to be excellent systems for the study of the complex interplay among temperature-dependence phase transitions, composition-dependent phase transitions, and superconductivity. Further experimental and theoretical work is essential to understand the behavior of these systems.

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