Normal and superconducting properties of K_xWO_3

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The resistivity, Seebeck coefficient, Hall coefficient, and superconducting transition temperature have been measured in K_xWO_3 for $0.20 \leq x \leq 0.32$ over the temperature rangee 1.5 to 375 K. The normal-state transport properties show temperature- and composition-dependent anomalies qualitatively similar to those observed in Rb_xWO_3, except that they occur at higher temperatures. This critical temperature has the same dependence on composition as observed in Rb_xWO_3. This behavior is in contrast to that of Cs_xWO_3 in which no anomalies are observed. The superconducting transition temperature also has the same general dependence on composition as in Rb_xWO_3, except it is lower for any given x value rising slowly as x decreases below 0.32, dropping to a minimum near $x = 0.25$, then increasing again as x decreases below 0.25.

I. INTRODUCTION

In previous work carried out in this laboratory it was shown that the normal electrical transport properties of hexagonal Rb_xWO_3 show anomalous properties while those of hexagonal Cs_xWO_3 do not.[1,2] Furthermore, both the superconducting transition temperature, T_c, and the temperature at which the normal-state anomalies occur in Rb_xWO_3 show a distinct change in composition dependence near $x = 0.25$. The conduction mechanism would be expected to be essentially the same in both materials and is believed to derive from a conduction band consisting of tungsten t_{2g} d orbitals interacting with oxygen $p\pi$ orbitals populated by electrons donated by the metal ions.[3] This would indicate that the differences in conduction properties are probably due to properties associated with the metal ion itself, e.g., size, mass, bonding, ordering, etc. In view of this, hexagonal K_xWO_3 was carefully studied. The K^+ ion is smaller and lighter than Rb^+ or Cs^+ and thus would be expected to be less tightly bound in the lattice.

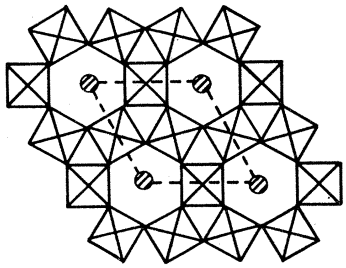

FIG. 1. Diagram of the hexagonal M_xWO_3 lattice structure viewed along the c axis. The M ion sites lie along the open hexagonal channels which are formed by corner linked WO_6 octahedra. The structure is filled at $x = 0.33$.

The crystal structure in the plane perpendicular to the c axis of the hexagonal tungsten bronzes is shown in Fig. 1. The channels have a radius of approximately 1.63 Å, and the Cs^+, Rb^+, and K^+ ions have radii of 1.69, 1.47, and 1.33 Å, respectively. The behavior of the normal and superconducting properties of Rb_xWO_3 and Cs_xWO_3 have been described in detail elsewhere[1,2] and will not be reproduced here.

II. EXPERIMENTAL METHODS

Single crystals of K_xWO_3 were grown by a solid-state reaction method similar to that described in detail previously.[1,2] The one difference was the necessary addition of a small amount of a halogen, presumably to act as a transport agent. While all the halogens except fluorine, which attacked the quartz growth tubes, produced crystals, it was found that optimum results in terms of quality, as measured by visual inspection and T_c, were obtained by the addition of 0.05 at.% KBr or RbBr to the starting materials. While crystals of Rb and Cs tungsten bronzes could be grown without the addition of a halogen, its presence facilitated the growth of these compounds; whereas it was essential for the growth of K_xWO_3 single crystals. The starting materials (M_2WO_4, WO_3, W, and MBr in ratios appropriate to the desired composition) were evacuated to 10^{-6} Torr and heated to 400 °C while pumping for 12 h. The reaction and crystal growth occurred in a sealed evacuated quartz tube held at 950 °C for five days. The crystals were shiny dark blue with the hexagonal habit, 3–10 mm in length and 30 to 300 μm across.

Due to the low energy of the K x-ray spectra, it was not possible to use the x-ray fluorescence method previously used for analysis of Rb_xWO_3 and

Cs_xWO_3 (Refs. 1 and 2) for K_xWO_3. However, the close agreement between the measured and nominal x values in the Rb and Cs compounds gives confidence that the nominal values of x are very close to the actual K concentrations of the K_xWO_3 crystals.

The resistivity and most of the T_c measurements were made using standard 4-lead dc methods. A large number of the T_c measurements were checked using the ac susceptibility method both on single crystals and on powder made from crushed single crystals. The Seebeck measurements were made by establishing a temperature gradient on crystals attached to two copper blocks with two Au-Fe-chromel thermocouples being used to measure the gradient. The methods used for all the electrical transport properties and the ac susceptibility were identical to those previously used for the Rb_xWO_3 and Cs_xWO_3 studies.[1,2]

III. EXPERIMENTAL RESULTS

The temperature dependence of the resistivity of K_xWO_3 is shown in Fig. 2 for $0.18 \leq x \leq 0.32$. The most striking feature of the data is the large, anomalous hump, which is very similar to that observed in Rb_xWO_3 except that the onset temperatures, T_B, are higher in K_xWO_3 below the highest concentration.[1] This is in contrast to Cs_xWO_3, in which no anomaly was observed.[2] T_B is plotted as a function of x for K_xWO_3 along with the previous data for Rb_xWO_3 in Fig. 3. The general behavior is the same in both materials with a maximum in T_B occurring near $x = 0.25$. It was not possible to extend the measurements above 400 K because the solder connections melted and the silver paint contacts were destroyed above this temperature.

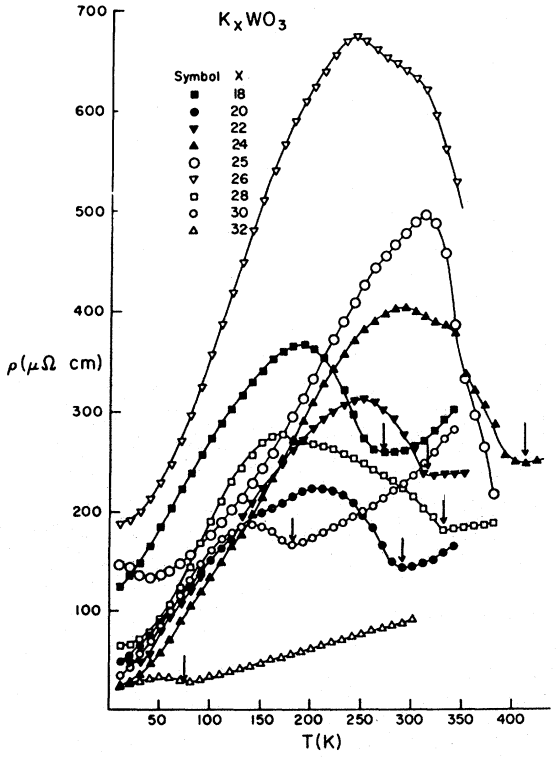

FIG. 2. Resistivity of K_xWO_3 as a function of temperature for various x values. T_B is the temperature at which the local minima occur and is indicated by the arows.

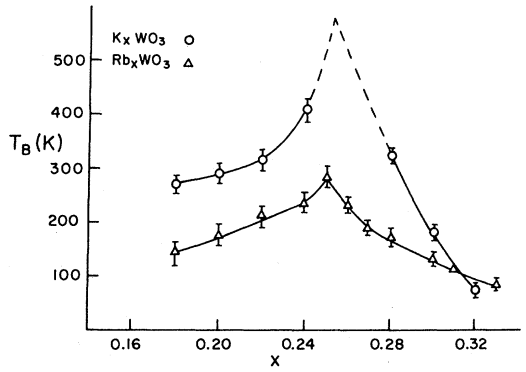

FIG. 3. Variation of the temperature T_B at which the onset of the high-temperature anomaly occurs for K_xWO_3 and Rb_xWO_3 (Ref. 1) as a function of x.

The Seebeck coefficients were measured over the entire concentration range $0.20 \leq x \leq 0.32$. The Hall coefficient could only be measured at $x = 0.20$, since only at this concentration did some crystals grow in the required platelet form. The resistivity, Seebeck coefficient, and Hall coefficients are plotted as a function of temperature in Fig. 4 for $x = 0.20$. As

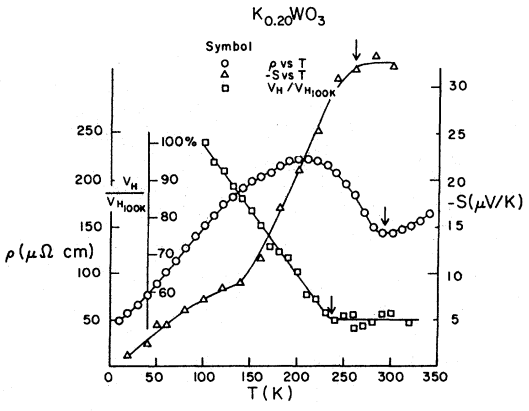

FIG. 4. Temperature dependences, of the resistivity, ρ, Hall voltage, and Seebeck coefficient, S, for $K_{0.20}WO_3$. This figure shows that the high-temperature anomaly is reflected in all three of these parameters. Arrows denote temperatures of transitions in behavior. The behavior is typical for all K concentrations < 0.33.

was found in Rb_xWO_3, an anomaly is observed in all three transport properties with the onset occurring at nearly the same temperature for all three.

Figure 5 shows the temperature dependence of the Seebeck coefficient for $0.18 \leq x \leq 0.30$. A sharp drop in the Seebeck coefficient is observed at a temperature designated as T_s. Above T_s the Seebeck coefficient appears to approach a constant value of about 32 μV/K, except for $x = 0.18$ and 0.30, where the value is about 20 μV/K. A peak in T_s is observed near $x = 0.25$ in agreement with that observed in the resistivity measurements. It should be noted that the temperature dependence of the Seebeck coefficient at low temperatures shows a distinctive variation in its concentration dependence. Between $x = 0.18$ and 0.25 it rises slowly with increasing temperature until $T = 150$ K, above which it increases much more rapidly before saturating around T_s. For $x > 0.25$, the Seebeck coefficient increases rapidly with increasing temperature beginning at the lowest temperature at which measurements were made ($\simeq 10$ K). Similar behavior has recently been observed in Rb_xWO_3.[4]

The superconducting transition temperatures for concentrations at which T_c was high enough to be measured (1.2 K) are shown in Fig. 6, along with previously reported data on Rb_xWO_3 and Cs_xWO_3.[1,2] Included also are some more recent data on Rb_xWO_3. The most interesting feature is that K_xWO_3 behaves

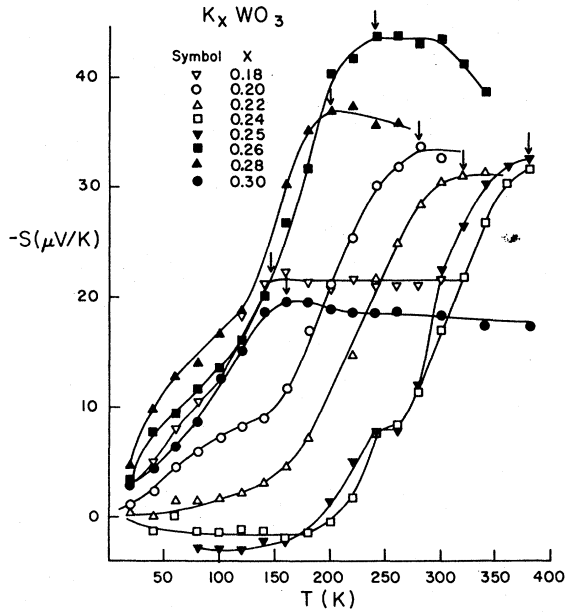

FIG. 5. Seebeck coefficient as a function of temperature for different compositions of K_xWO_3. Arrows denote critical temperature, T_s. Note that the low-temperature behavior of the Seebeck coefficient is different for $x > 0.25$ than it is for $x < 0.25$.

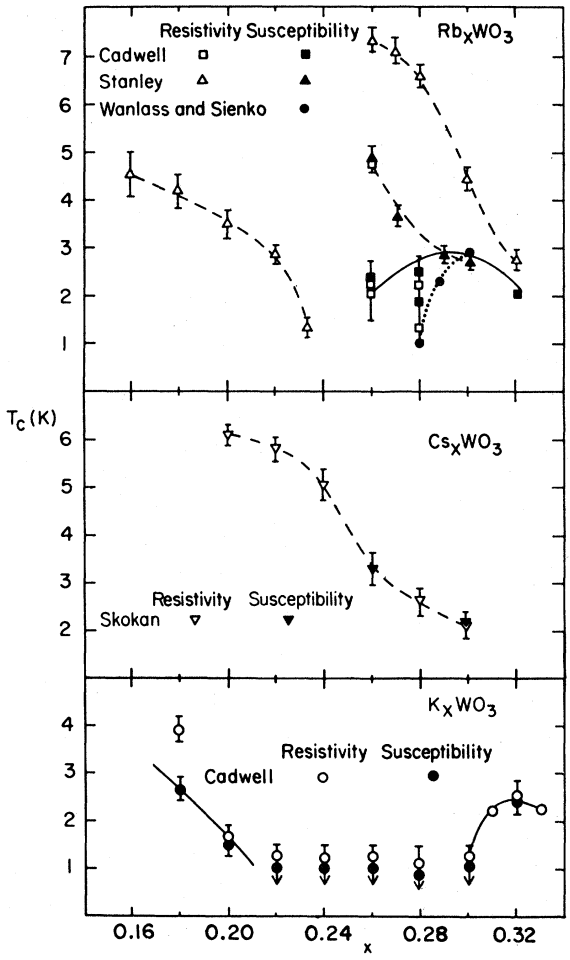

FIG. 6. Superconducting transition temperature, T_c, as a function of x for K_xWO_3, Rb_xWO_3 (Ref. 1), and Cs_xWO_3 (Ref. 2).

very much like Rb_xWO_3, except the T_c's are lower at all concentrations below $x = 0.33$. The minimum in T_c near $x = 0.25$ is an interesting feature of both materials. The large variation in T_c for $0.25 \leq x \leq 0.33$ in Rb_xWO_3 for different batches of crystals grown in the same way still presents an enigma. All K_xWO_3 samples which displayed superconductivity showed a large 60° anisotropy in H_{c_2} in the plane perpendicular to the c axis and a 180° anisotropy in a plane containing the c axis similar to that observed in Cs_xWO_3 and Rb_xWO_3.[1,2]

IV. DISCUSSION

The most significant aspect of these experimental results is that they provide further evidence that the anomalous normal transport and superconducting properties of the hexagonal tungsten bronzes are pri-

marily dependent on the character of the metal ion. The similarity in properties of the Rb and K compounds indicates that the Rb^+ and K^+ ions possess common characteristics not possessed by the Cs^+ ion which produce the anomalous characteristics. It seems highly likely that these anomalies are associated with some type of phase transition.

The transition temperature for the same metal ion concentrations is generally significantly higher in K_xWO_3 than in Rb_xWO_3, but it is interesting that both compounds show a maximum in T_B near $x = 0.25$. This would indicate that this composition is the most conducive to formation of the low-temperature phase and that the change in behavior at $x = 0.25$ is not due to qualitative differences in properties between the K^+ and Rb^+ ions.

The question of the kind of phase change which could produce these anomalies cannot be answered from the current data; however, from the systematics of the alkali-metal hexagonal tungsten bronze system the possibility of certain models can be suggested and some conclusions can be drawn. There is considerable evidence[3] that the conduction mechanism and band structure in all the alkali metal tungsten bronzes is primarily associated with the tungsten t_{2g} and oxygen $p\pi$ orbits in the WO_3 octahedral lattice. Assuming this is true, the behavior of K_xWO_3 would appear to strengthen the argument that the variation in the transport properties of the alkali hexagonal tungsten bronzes is due to properties of the metal ion itself. In moving up the periodic table, one goes from no transition in Cs_xWO_3, to a phase transition in Rb_xWO_3, to a phase transition at higher temperatures in K_xWO_3. In addition, recent measurements of the resisitivity of mixed crystals of $Cs_xRb_yWO_3$ for $0.20 < x + y < 0.30$ as a function of temperature[5] have indicated that the transition decreases in temperature and possibly broadens as the Cs concentration increases before disappearing at high Cs concentrations. The obvious first choice for the controlling parameter is the size of the ions. It is already known that metal ion size plays a significant role in determining the crystal structure of the WO_3 lattice in the tungsten bronzes. In going from the large Cs^+ ion to the smaller K^+ ion the ions become much smaller than the "holes" in the hexagonal channels where they reside giving them greater mobility and less interaction with the lattice. Specific-heat studies[6] indicate that the coupling constant of the Cs^+ ions to the lattice is more than twice that of the smaller Rb^+ ions. Although the variation in transport properties cannot be absolutely ascribed to ion size since there are other parameters which scale in the same manner, e.g., ionization potential, it does appear to be the most appealing of the choices.

While the correlation of the transport properties with ion characteristics would seem to be well established, the detailed mechanism is still not clear. One possibility of course is that there exists an alkali-ion-concentration-dependent crystallographic phase change for which a change in the Fermi surface occurs. The resistivity and Hall coefficient indicate a decrease in the number of carriers in the low-temperature phase. However, x-ray-diffraction studies show no abrupt changes in the lattice parameters as a function of temperature to an accuracy of better than 0.0025 Å.[7,8] It is possible that a distortion smaller than this could result in the observed property changes particularly if the Fermi surface lies in a region of a rapidly changing density of states as it is proposed to do in the tetragonal tungsten bronzes[9]; however, the lack of observation of the distortion plus the broadness of the transition and the continuous change in the transport properties below the transition seem to indicate a different type of mechanism.

Other mechanisms can be considered such as a transition from a high-temperature uncorrelated motion of the insertion metal ions in the channels to a low-temperature correlated motion or the formation of a charge density wave (CDW). The transition from uncorrelated to correlated motion could result in resistivity behavior such as that observed; however, the increase in transition temperature with decreasing concentration would require the coupling energy between the insertion ions to increase with decreasing x which seems very unlikely.

The behavior of the transport properties with temperature is very similar to that of other systems in which the formation of CDW has been confirmed[10]; however, again it is difficult to understand the behavior of T_B with x since in general disorder tends to drive the CDW transition down in temperature. The observed behavior could be explained if a softening of the lattice with decreasing alkali concentration results in an enhanced electron-phonon interaction[11]; however, no other data exist which can support this idea. Ordering of the Rb^+ and K^+ ions near $x = 0.25$ could in some way play a role either in the formation of the CDW or otherwise. To date there is no evidence for such ordering in the x-ray diffraction experiments, but since the x-ray line intensity of Rb would be only 1% of the strongest W line, it is possible that the work done so far has not been done with sufficient care to observe such ordering. Ordering has apparently been observed in cubic Na_xWO_3 near $x = 0.75$.[12]

The cause of the transition which occurs with concentration in both the K_xWO_3 and Rb_xWO_3 compounds near $x = 0.25$ is just as unclear as the mechanism for the transition with temperature discussed above. In addition to the observed changes in the transport properties, the superconducting transition temperatures also reflect this phase change with both K_xWO_3 and Rb_xWO_3 showing a minimum in T_c near $x = 0.25$. If one compares the lower T_c's of the K_xWO_3 system with the higher values of T_B for

Rb_xWO_3, i.e., greater stability of the low-temperature phase for K_xWO_3, reaffirmation is given to the contention made earlier[1] based on the Rb_xWO_3 data that the more stable the low-temperature phase the lower the T_c. In Cs_xWO_3 no anomaly in the transport properties occurs, which presumably indicates there is no transition to the low-temperature phase, and in general the T_c's are higher. Studies of the mixed crystals $Rb_xCs_yWO_3$ for $0.20 < x+y < 0.30$ have shown that T_c scales approximately linearly with Rb to Cs concentrations between the values of T_c for pure Rb_xWO_3 and Cs_xWO_3, which when compared to the behavior of T_B in these same compounds is in agreement with the above picture.

Such a relationship between superconducting T_c's and higher temperature phase transitions have been observed in a number of superconducting systems, particularly in the $A15$ structures[13] where observable crystallographic distortions occur. However in the K_xWO_3 and Rb_xWO_3 systems no symmetry changing distortion is observed in this concentration range; rather the lattice parameters appear to change linearly with concentration although there is significant scatter in the data, particularly for the K compounds.[14] The observed behavior of the T_c's is also consistent with the high-temperature transition being a CDW transition since such an inverse relationship of critical temperatures has been observed in superconducting CDW systems[15]; however this still would not answer the question of the extremal behavior near $x = 0.25$. The behavior of the T_c's and T_B's would seem to possibly indicate some unique condition near $x = 0.25$ which results in the observed behavior, such as the ordering mentioned above. The fact that the critical concentration is approximately the same for both the Rb and K compounds could support the ordering concept. The behavior of the Seebeck coefficient indicates a real difference between the high- and low-concentration phases in both K_xWO_3 and Rb_xWO_3.

V. SUMMARY

While we have been unable to find the exact qualitative model consistent with the interesting behavior of the transport and superconducting properties of the hexagonal tungsten bronzes, the data indicate that properties of the insertion ion, perhaps size, play the key role in the properties of these materials. For insertion ions which fit relatively loosely in the channels, there is evidence of high- and low-temperature phases and also some type of subtle phase change with composition near $x = 0.25$. On the other hand, for large insertion ions which are more tightly bound in the channels, there is little or no evidence for any phase changes.

Clearly, further work is necessary to establish the mechanisms which produce the phenomena observed in these systems. Higher-resolution crystallographic studies are currently in progress in hope of identifying clearly the lattice dynamics around T_B.

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