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Evidence of structural phase transitions in superconducting Rb_xWO_3

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In the hexagonal tungsten bronze Rb_xWO_3, the ordering of the vacancies of the Rb sites has been observed by neutron diffraction measurements. This ordering is the cause of the resistivity anomaly observed by Stanley *et al.* Another type of structural transition has also been found for the samples with $x < 0.25$. The results give support to the speculated correlation between the superconducting transition temperature and a structural phase transition.

In the hexagonal tungsten bronzes M_xWO_3, the M atoms are located in the large open channels along the c axis formed by the WO_6 linkage.[1] For $M_{0.33}WO_3$, all of the M atom sites are filled. Each M atom contributes one electron to the conduction band of the WO_6 skeleton and this band is believed to be nearly independent of the species of M atoms.[2] The difference in the phonon structure may be important for the difference in the superconducting transition temperatures of M_xWO_3 for different species of M atoms with a fixed x value. Specific-heat measurements[3,4] have shown that there is an Einstein-like mode in M_xWO_3, and this local mode has been directly observed in $K_{0.33}WO_3$,[2,5] $Tl_{0.33}WO_3$,[2] and $Rb_{0.3}WO_3$.[6] Kamitakahara *et al.*[2] have shown a close correlation between the superconducting transition temperature T_c and the energies of the local modes of the M atoms in $M_{0.33}WO_3$.

The x dependence of T_c in Rb_xWO_3, K_xWO_3, and Cs_xWO_3 has been studied by Stanley *et al.*,[7,8] Cadwell *et al.*,[9] and Skokan *et al.*,[10] respectively, where the former two series of materials show quite characteristic behavior, as shown for Rb_xWO_3 in the insert in Fig. 1. They have also found a resistivity anomaly at a temperature T_B much higher than T_c. The x dependence of T_B is closely correlated with the superconducting T_c as shown in Fig. 1. These authors speculated the possibility of structural transitions, such as that resulting from the formation of a charge-density wave, which may have a large effect on the energy of the local mode of the M atoms. They mentioned that the x-ray studies have failed to see any evidence of this phase transition.[11]

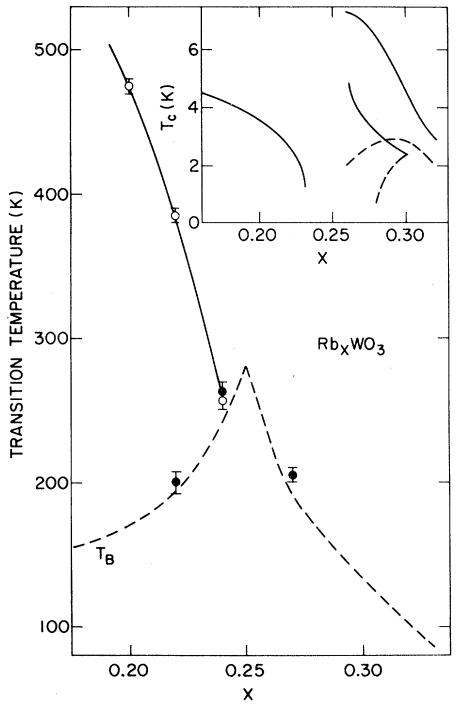

FIG. 1. Phase transition temperatures in the Rb_xWO_3 system. Solid circles: structural transition temperatures T_S; open circles: structural transition temperatures T_S'; dashed line: resistivity anomaly T_B as determined by Stanley *et al.* (Refs. 7 and 8). The insert shows the x dependence of the superconducting transition temperature T_c. For $x > 0.25$, conflicting results were reported as shown in the figure (see Refs. 7 and 8).

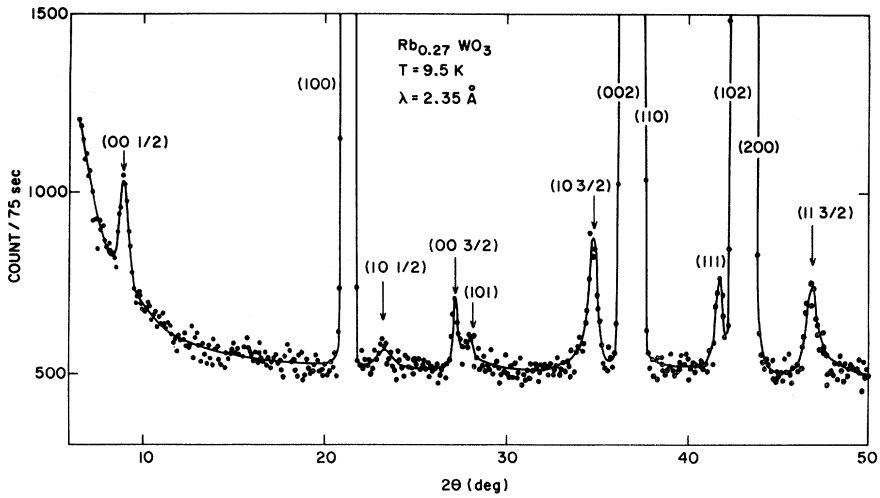

FIG. 2. The powder diffraction pattern taken at about 10 K for $Rb_{0.27}WO_3$. The peaks with arrows disappear at $T_S = 205$ K.

In this Communication, the preliminary results of neutron measurements will show evidence of the structural phase transitions in Rb_xWO_3. The measurements have been carried out on a triple-axis spectrometer at the High Flux Beam Reactor at Brookhaven National Laboratory. The samples were prepared by solid reaction of a mixture of the proper amounts of WO_3, W, and Rb_2WO_4 sealed in a quartz tube. Figure 2 shows the neutron powder-diffraction pattern of $Rb_{0.27}WO_3$ at 10 K. The peaks indicated by the arrows disappear in the high-temperature phase above $T_s = 205$ K. The other peaks are the fundamental peaks of the high-temperature structure. The temperature dependence of the peak intensity of the (1,0,1.5) superlattice point is shown in Fig. 3. The structural transition temperature T_S agrees reasonably well with T_B, the temperature of the observed resistivity anomaly.[7,8] For the sample with $x = 0.27$, all of the superlattice peaks can be indexed assuming a doubling of only the c axis. The intensity distribution suggests that these are due to the ordering of the Rb atoms along the c direction. Since the doubled unit cell contains four Rb sites, $x = 0.25$ corresponds to exactly one vacancy per unit cell. This condition may be important, as suggested by Stanley *et al.*,[7,8] for the characteristic x dependences of T_c and T_B (or T_S).

We have also studied four additional samples with x values of 0.20, 0.22, 0.24, and 0.33. For the samples with $x = 0.22$ and 0.24, we have observed the appearance of superlattice peaks at temperatures close to the values of T_B determined by the resistivity measurements. For the $x = 0.20$ and 0.33 samples, no clear evidence of this type of transition has been observed.

Another set of superlattice peaks which appear at a temperature T_S' has been observed for samples with $x < 0.25$. This transition involves the doubling of the lattice constant within the c plane. The transition temperatures are shown in Fig. 1 by the open circles. The intensities of these superlattice lines show systematic changes with composition, and model calculations are now being carried out to establish the ordering schemes.

It is very tempting to speculate that these structural transitions are correlated with the superconducting transition temperatures. Possible causes are as follows: (a) The effect of the phase transition on the atomic (hopping?) motion may play an essential role as in the case of the local structural instability discussed by Ngai and Reinecke[12] and Silberglitt and

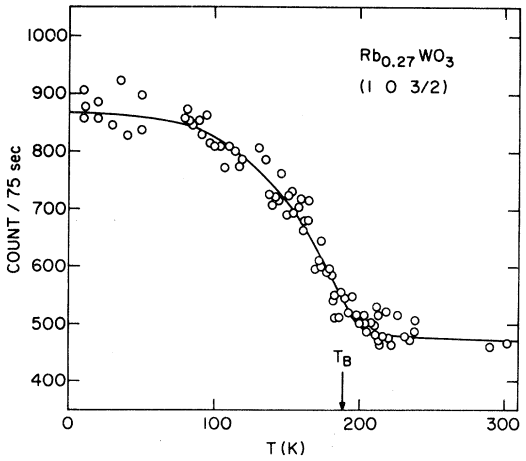

FIG. 3. The temperature dependence of the intensity of the 10 1.5 superlattice point. The value of T_B determined by Stanley *et al.* (Refs. 7 and 8) is shown by the arrow.

Nosanow.[13] (b) The electronic structure may be changed by the appearance of the new ordering in a way similar to the case of a charge-density wave transition. A gap may develop at some part of the Fermi surface which may explain the resisitivity anomaly. (c) The energy of the low-lying local mode of the Rb atoms may change as a result of the transition. Using the inelastic scattering from the powder samples, we can directly observe a large peak in the spectrum due to the local modes of the Rb atoms. The peak energy at room temperature does not exhibit any appreciable correlation with T_c as x is changed. We are presently studying the temperature dependence of this peak in the $x=0.27$ sample.

We have also found evidence of structural phase transitions in K_xWO_3, which will be discussed later together with the more detailed structure determination in the distorted phases of the Rb compounds.

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