

Percolation View of Transport Properties in Na_xWO_3 †

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New measurements of electrical conductivity and Hall constants have been performed on single crystals of Na_xWO_3 for $0.22 < x < 0.63$ and temperatures from 1.2 to 300 K. The conductivity varies with x according to the relation, $\sigma \propto (x - x_c^*)^{1.8 \pm 0.2}$, in agreement with calculations of Kirkpatrick for a related model system. The value of the constant x_c^* is determined to be 0.16 ± 0.03 , consistent with a percolation model based on the degree of orbital connectivity between occupied sodium sites via tungsten orbitals.

The behavior of the electrical conductivity in a disordered system which can be usefully described in terms of percolation theory is of considerable current interest. In particular, Last and Thouless¹ and Kirkpatrick² have obtained results for the conductivity as a function of density of conducting elements for densities near the insulator-metal transition in such systems. Kirkpatrick used a model consisting of an array of low-resistance links located randomly on a simple cubic structure of lattice points. His computer calculations of the conductivity σ as a function of p , the probability that any given pair of first-nearest neighbors is connected by a link, gives

$$\sigma \propto (p - p_c)^{1.5 \pm 0.2}, \tag{1}$$

where p_c is the critical occupation probability at which conduction first appears. This expression is expected to be valid only for p near p_c . Although the particular exponent of Eq. (1) is derived for the simple cubic lattice, it is not expected to depend strongly upon the details of the lattice structure.

We have measured the dc electrical conductivity of single crystals of Na_xWO_3 at helium temperatures and for values of x near a transition from metallic to insulating behavior. We have fit these data to an expression analogous to Eq. (1), namely,

$$\sigma \propto (x - x_c^*)^\beta, \tag{2}$$

where x_c^* is a critical sodium concentration for the appearance of electrical conduction at low temperature. Figure 1 displays our data as well as earlier data summarized by Shanks, Sidles, and Danielson.³ The set of nine data points is graphed in a log-log plot as a function of $(x - x_c^*)/x_c^*$ for several different choices of x_c^* . It is seen that for $x_c^* = 0.17$ the power-law dependence is followed for the set of crystals from $x = 0.22$ to 0.63 . The error bars shown represent the relative uncertainty of the sodium concentration within each of the samples. Systematic error in determination of the

concentration is estimated to be ± 0.02 . To account for this error, plots of the data of Fig. 1 were made with the values of x systematically raised and lowered by increments of 0.02 about their central values. From these plots, a value of $x_c^* = 0.16 \pm 0.03$ is obtained with $\beta = 1.8 \pm 0.2$.

For reasons which we discuss more extensively below, we would expect the Na_xWO_3 system to be a rather good embodiment of Kirkpatrick's resistor model. The results from Fig. 1 give credence to some generality of his results and also extend our knowledge about the Na_xWO_3 system. In the remainder of this paper, we will examine the implications of the data and analysis presented in Fig. 1 and of Hall-constant measurements made by us and others. This examination is developed in terms of a percolation model for the transport

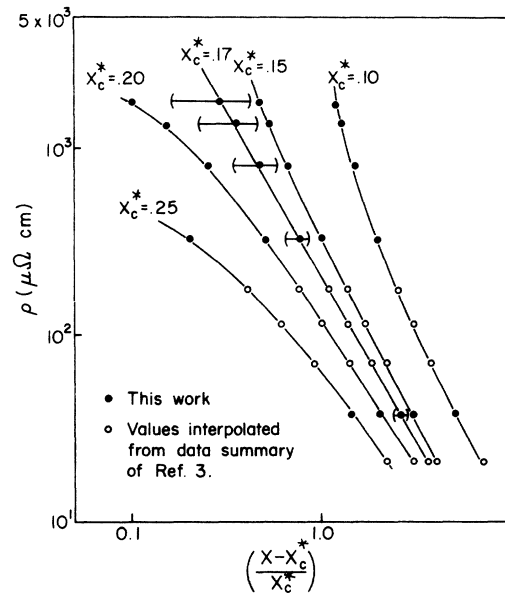


FIG. 1. Log-log plot of resistivity as a function of $(x - x_c^*)/x_c^*$. In the several curves, x_c^* is varied, seeking a straight-line fit.

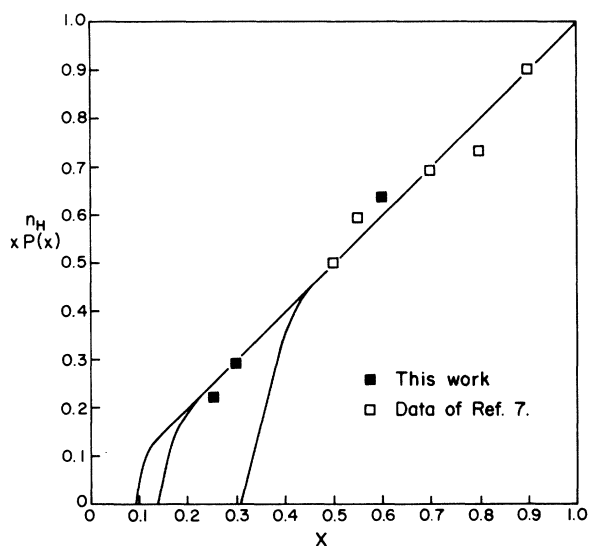


FIG. 2. Comparison of observed number of Hall carriers, n_H , in crystals of cubic Na_xWO_3 , to calculated values of $xP(x)$ with $x_c = 0.097$, 0.137 , and 0.307 .

properties of Na_xWO_3 for values of x near x_c .

Fuchs⁴ proposed a simple first-nearest-neighbor percolation model for Na_xWO_3 . His model is in agreement with the fact that the experimentally derived density of conduction-electron states is directly proportional to the sodium concentration x for $x > 0.5$. Domb and Dalton⁵ have calculated the critical probability p_c for site percolation on a simple cubic lattice for linkages to first-nearest neighbors only ($p_c = 0.307$), for first- and second-nearest-neighbor linkage ($p_c = 0.137$), and for first-, second-, and third-nearest-neighbor linkage ($p_c = 0.097$). Applying the percolation model to Na_xWO_3 , the occupation probability p should correspond to x , provided the sodium ions are located at random on the appropriate vacancy sites in the WO_3 structure. Thus, the Fuchs model would give the insulator-metal transition at $x = 0.307$. Earlier observations at nitrogen and room temperature³ indicated that the transition might occur at a somewhat lower sodium concentration. As mentioned above, our conductivity analysis gives a concentration $x_c^* = 0.16$, which appears to fall slightly above the value expected for the first- and second-nearest-neighbor linkage case.

Hall-constant measurements give additional information concerning the dc electronic conduction. The number of electrons that can participate in dc conduction will be given by

$$n = pP(p) = xP(x), \quad (3)$$

where x is the probability that any given sodium site is filled and $P(x)$ is the probability that the

site is located in an unbounded cluster of filled sites. Holcomb and Rehr,⁶ for the case of highly doped semiconductors, hypothesized that the n given in Eq. (3) may be approximated by using the number of Hall carriers obtained from measurements of R_H and the single carrier relation,

$$1/R_H = n_H e c. \quad (4)$$

We have measured R_H for some of the samples for which conductivity data is given in Fig. 1. Figure 2 graphs the values of n_H obtained from these and earlier measurements of R_H ⁷ and the use of Eq. (4). The curves are values of $xP(x)$ calculated⁸ for the three cases: first-nearest-neighbor linkage; first- and second-nearest-neighbor linkage; and first-, second-, and third-nearest-neighbor linkage. The data for n_H appear to exclude a percolation model based on first-nearest-neighbor linkage only. Unfortunately, crystal preparation and Ohmic-contact difficulties are such that measurements of R_H have not been obtained at concentrations sufficiently low to distinguish between the two other curves for $xP(x)$.

We believe that the correct value of x_c for Na_xWO_3 is probably 0.10, corresponding to first-, second-, and third-nearest-neighbor linkage. That value, as well as the value of 0.16 for x_c^* obtained from the conductivity analysis, can be understood by considering the wave functions of an electron bound to a filled sodium site.

Sienko⁹ has proposed a model for Na_xWO_3 in which the charge transport is attributed to delocalized electrons contributed by the sodium atoms occupying a conduction band formed from tungsten $5d(t_{2g})$ orbitals. There is independent evidence supporting this orbital assignment.^{10,11} However, for an isolated sodium impurity, the donated electron would be electrostatically bound by the sodium ion. Hence, the electron should occupy primarily the $5d(t_{2g})$ orbitals on the eight adjacent tungsten ions, rather than occupy a delocalized band state. (In the cubic form of Na_xWO_3 , the WO_3 structure is simple cubic perovskite, and the sodium ions occupy the cavities formed in the middle of a cube formed by eight tungsten ions at the corners and twelve oxygen ions at the midpoints of the cube edges.)

The electrostatic polarization of the $5d(t_{2g})$ orbitals leads naturally to the assumption that charge transfer between two sodium sites will only occur if the sites are in contact via shared tungsten $5d(t_{2g})$ orbitals. For first-nearest-neighbor sodium sites, there will be four tungsten atoms whose $5d(t_{2g})$ orbitals will be populated from the two sodium sites. Second-nearest-neighbor sodium sites will share the orbitals of two tungsten atoms and third-nearest neighbors will have the orbitals of only one tungsten atom in common.

Fourth-nearest neighbors will not have any tungsten $5d(t_{2g})$ orbitals in common, nor will those of any more distant separation. Hence the Na_xWO_3 system can be described by a site percolation model wherein charge may percolate from any occupied sodium site to any other occupied sodium site that is a third-nearest neighbor or closer. Thus, one would predict the value for x_c to be 0.097 from the Domb and Dalton⁵ calculation.

How do we then account for the value $x_c^* = 0.16$? We postulate that this value is obtained from the conductivity-data analysis of Fig. 1 because of the fact that the orbital linkages to second- and third-nearest-neighbor sites are weaker than to the first-nearest-neighbor sites. For a Kirkpatrick-like model, with the first-, second-, and third-nearest neighbors connected by equal-value resistors, one would expect to have the value $x_c^* = 0.097$ in Eq. (2). But to represent the Na_xWO_3 case, the resistors connecting linked sites should vary because of the different degrees of orbital linkage. Domb and Dalton⁵ have shown how the value of x_c would depend upon the coordination number of the site lattice. For Na_xWO_3 , we introduce an effective coordination number z^* , which is obtained by a weighted counting of the bonds leaving a site. The weighting factor will be the effectiveness of the bond in contributing to the conduction process. From a given starting site, there are six bonds to the six first-nearest-neighbor sites. The bonds to the twelve second-nearest-neighbor sites have orbital linkages that are one-half as effective. Thus, the weighted number of bonds from the initial site to the second-nearest-neighbor sites is taken to be 6. The bonds to the eight third-nearest neighbor sites have linkages that are one-quarter as effective as for first-nearest neighbors, resulting in two weighted bonds. The effective coordination number z^* is taken to be the sum of the three sets of weighted bonds 6, 6, and 2, or 14. For $z^* = 14$, Domb and Dalton's calculations lead to a value of 0.18 for x_c^* . The good agreement of this value with the empirical value of 0.16 from the data analysis of Fig. 1 should not be taken too seriously, but it does suggest we may be on the right track.

There must, of course, be a single value for x_c in the percolation model, and our picture would suggest that this value is 0.097. Our interpretation of the existing conductivity data leads to the natural presumption that if one were able to make single cubic crystals for x values below $x = 0.22$, he would find the conductivity data breaking away from the straight-line plot of Fig. 1 with conductivity finally dropping to zero only as x neared 0.10. If low-concentration crystals were obtainable and Hall-constant measurements could be made, our model would predict that the values of

n_H plotted in Fig. 2 should follow down the $xP(x)$ curve which intercepts at $x = 0.097$.

Our crystals were obtained by a diffusive dilution process, similar to that employed by McNeill and Conroy.¹² First, single crystals of cubic Na_xWO_3 with $x = 0.6$ were prepared electrolytically from a fused melt of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and WO_3 . A crystal of $\text{Na}_{0.6}\text{WO}_3$ of approximate dimensions $0.7 \times 1 \times 5$ mm was then placed in a quartz tube and surrounded by a powdered mixture of $\text{Na}_{0.6}\text{WO}_3$ and a suitable fraction of WO_3 . The tube was evacuated and heated to 925°C for 10 to 14 days, then quenched to room temperature. The excess sodium in the $\text{Na}_{0.6}\text{WO}_3$ diffuses into the WO_3 , resulting in equilibrium being established between the powder and crystal at a lower value of x . The quenching is done in an attempt to obtain a metastable cubic structure at room temperature. Values of x were determined by chemical analysis, by determining x-ray lattice constants (using the calibration of Straumanis¹³), and by electron-microprobe analysis, using x-ray fluorescence. For crystals with $x \approx 0.30$, the local sodium concentration in a given crystal varied by $\pm 10\%$. At concentrations near $x = 0.20$, uniformity was poorer, with about $\pm 20\%$ variation in local concentration. We have been unable to obtain good crystals with $x < 0.20$, probably because we are attempting to lower the sodium concentration too far below the range of x values in which the cubic structure is thermodynamically stable at room temperature.

We now comment on the consistency of our model and our value, $x_c^* = 0.16 \pm 0.03$, with previous work. The cell-percolation model naturally preserves the direct proportionality of density of states to the value of x for $x > 1.4x_c$. The nuclear-magnetic-resonance data^{10, 11, 14-16} have been shown to be consistent with the assumption that the conduction electrons reside in tungsten $5d(t_{2g})$ orbitals. The NMR properties can not readily distinguish between a genuine conduction band and the percolating cluster model, because these properties are primarily determined by local electron characteristics.¹⁷

The optical data¹⁸ show a major change in the shape of the absorption spectra between $x = 0.20$ and $x = 0.15$ for Na_xWO_3 . This change is consistent with our value, $x_c^* = 0.16$.

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¹⁷At sufficiently high values of x , it is not clear that a percolation model is substantially different from a delocalized-band model. At high x values, most occupied sites will also have their first-nearest-neighbor sites filled, with the localized electron charge distributions now forming a uniform electron gas modulated by the periodicity of the lattice. Thus a delocalized band model having tungsten $5d(t_{2g})$ characteristics may adequately describe many of the properties for $x \gg x_c$.

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