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Transport properties of cubic Na_xWO_3 near the insulator-metal transition*

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We have extended previous measurements of electrical resistivity and Hall coefficient of single crystals of cubic Na_xWO_3 to a wider range of values of x and of sample temperature. These new data cover a temperature range from 4.2 to 300 K, and a range of x values from $x = 0.22$ to 0.30.

There exist in the literature a number of reports of previous measurements of electrical resistivity, ρ, and Hall coefficient, R_H, for single crystals of Na_xWO_3. Mühlestein and Danielson[1] reported a particularly complete and careful set of measurements of cubic crystals in the range of x values from $x = 0.40$ to 0.90. Measurements of ρ at lower values of x were made by McNeill and Conroy[2] for temperatures between 77 and 400 K. Lightsey[3] extended these measurements of ρ to the He temperature range, and extended room-temperature measurements of R_H for x values down to $x = 0.25$. We report here additional data which extend the range of R_H measurements in both variables, x and T, and provide further information on the temperature dependence of ρ for the samples with $x < 0.30$. We then collect all existing data into several plots.

Our interest in this work has stemmed from a desire to investigate the nature of the metal-insulator transition in this system, which is centered at an x value of about 0.25.

EXPERIMENTAL NOTES

Methods of preparation and analysis of our samples were described in Ref. 3. A straightforward four-probe method was used for the dc resistance measurements. For the Hall measurements, a five-probe method is used. That is, one of the voltage probes is, in fact, a pair of probes with a variable tap between the two members of the pair for the purpose of balancing the voltage across the crystal to null at zero magnetic field.

Making good electrical contact to the crystals becomes increasingly difficult as the x value decreases. Our most reliable method consisted of plating copper-film electrodes onto the Na_xWO_3 crystals by the Dalic plating method,[4] then subsequently attaching voltage and current leads to these copper spots by means of pure indium solder.

RESULTS

New data for electrical resistivity at room temperature are given in Fig. 1, along with those of Refs. 1–3. Figure 2 plots data as a function of $1/T$ for samples at various values of x. Figure 2 makes it particularly clear that thermal activation of a portion of the carriers appears for $x \leq 0.25$. Figure 3 displays new data for R_H, as well as the data of Refs. 1 and 3. All points were measured at room temperature except for the two points noted on the graph. Again, as with the resistivity data, a partial freezeout of Hall carriers appears for $x < 0.25$.[5]

In Table I, we tabulate all relevant data collected in our laboratory. We include calculated values of the Hall mobility, μ_H, defined as R_H/ρ.

Data from this laboratory are in generally good agreement with that of Refs. 1 and 2. There is one noticeable discrepancy with the data of McNeill and Conroy. The temperature dependence of ρ for

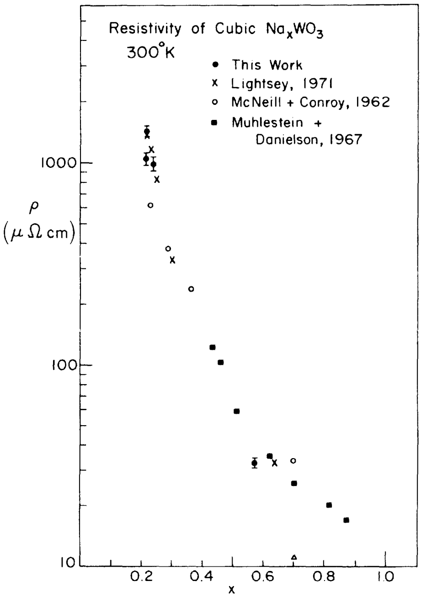

FIG. 1. Semilog plot of resistivity of cubic Na_xWO_3 as a function of x at $T = 300$ K. Data of McNeill and Conroy (Ref. 2), of Lightsey (Ref. 3), and representative points from the data of Mühlestein and Danielson (Ref. 1) are shown as well as our data.

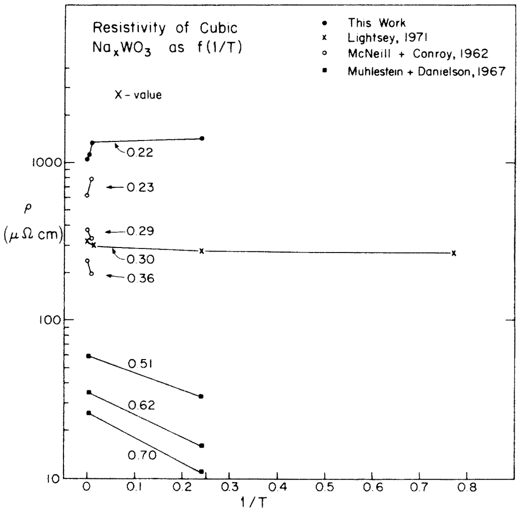

FIG. 2. Data for resistivity at several temperatures are shown for various single-crystal samples of cubic Na_xWO_3 used by McNeill and Conroy, by Mühlestein and Danielson, by Lightsey, and in the present work.

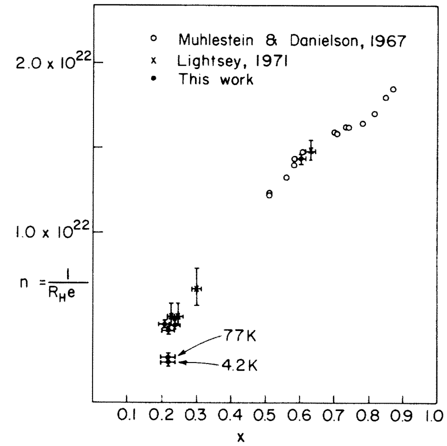

FIG. 3. Measurements of relative number of Hall carriers, $n_H = 1/R_H e$, are displayed as a function of x. Data of Mühlestein and Danielson (Ref. 1) and of Lightsey (Ref. 3) are shown as well as our own data. All data shown were taken at room temperature except the two values for the sample at $x = 0.22$, which were measured at the temperatures labeled.

TABLE I. Tabulation of our data on transport properties of cubic Na_xWO_3 (includes some data given in Ref. 3).

x value	T (K)	ρ ($\mu\Omega$cm)	R_H [a] (10^{-3} cm^3/C)	$\mu_H = R_H/\rho$ (cm^2/V sec)
0.63± 0.01	300	33.6± 5%	0.42	12.5
	77	21.0	0.42	
	4.2	19.6	0.47	
0.57	300	32	0.49	15.3
0.30	300	326	0.94 ± 0.15	2.9
	77	299	1.23 ± 0.2 [b]	
	4.2	283	1.48 ± 0.3 [b]	
	1.3	270	1.55 ± 0.5 [b]	
0.25	300	804	1.23 ± 0.15	1.5
0.24	300	961	1.36	1.4
0.23	300	1125	1.26	1.1
0.22	300	1333	(1.95)	
0.22	300	1027	1.27 [c]	1.2
	195	1100	1.52	
	77	1300	1.92	
	4.2	1430	2.25	
0.21	300	1400	1.45	1.0

[a] Estimated uncertainty ±8% except as otherwise noted.

[b] This datum is not plotted in Fig. 3. The large experimental uncertainty in this early Hall datum stems from difficulties with the maintenance of good electrical contacts at low temperatures. The datum does apparently show a decrease in the number of Hall carriers with decreasing temperature. However, its credibility is on a substantially lower level than the temperature-dependent datum plotted in Fig. 3 for the sample at $x = 0.22$, taken with the improved probe attachment method noted in this paper.

[c] This data point is not plotted in Fig. 3 in order to reduce congestion on graph.

our samples at and below $x = 0.25$ appears to match the temperature dependence of their $x = 0.23$ sample, whereas the magnitude of the resistivity for their $x = 0.23$ sample would place it at about $x = 0.26$ in our scale of ρ as a function of x. This discrepancy cannot be entirely accounted for by errors in x determination in either our samples or theirs, since the match of magnitude of ρ and temperature dependence thereof is somewhat inconsistent.

DISCUSSION

Extended discussion of the implications of this transport data near the metal-insulator transition is inappropriate for this short a paper. Moreover, the rather coarse grid of values of x and T will clearly not permit testing of any theoretical model of the metal-insulator transition in cubic Na_xWO_3 in fine detail. We can, however, comment on what seem to us to be a few key points in the data.

(a) The temperature dependences of ρ and R_H both suggest that partial localization of conduction electrons appears at low temperatures for $x \leq 0.25$.

(b) For crystals with $x > 0.25$, a model in which electrons freed from Na atoms fill a rigid band with shape similar to the conduction band of[6] ReO_3 has been suggested.[7-9] The room-temperature data of Fig. 3 appear to be consistent with such a model, since no substantial deviation from the condition $n_H = x/a^3$, where a is the cubic-cell edge length, is visible. This conclusion is consistent with implications of recent data for electronic specific heat and magnetic susceptibility obtained at low x values by Zumsteg.[8]

(c) We have found it impossible to retain the cubic structure in crystals with $x < 0.22$. So far as we know, no M_xWO_3 crystal with any ion M has been found to exhibit the cubic or pseudocubic structure unless it is also true that ρ exhibits metallic behavior.

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[2] W. McNeill and L. E. Conroy, J. Chem. Phys. 36, 87 (1962).

[3] P. A. Lightsey, Phys. Rev. B 8, 3586 (1973).

[4] The Dalic process is a method of brush electroplating of localized areas without the use of immersion tanks. Details of our use of the method are given in the M.S. Thesis of D. A. Lilienfeld (Cornell University, 1975) (unpublished).

[5] Earlier measurements of R_H, taken with a more primitive probe attachment arrangement, showed some temperature dependence of R_H in the samples at $x = 0.23$, 0.25, and 0.30. However, we have not included these earlier data—we believe them to be unreliable because of excessively high-voltage probe resistances which sometimes occurred with the earlier method of probe attachment.

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