

Heat capacity and magnetic susceptibility of Na_xWO_3 †

F. C. Zumsteg*

Laboratory For Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

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Measurement of the specific heat and magnetic susceptibility of the cubic sodium tungsten bronzes, Na_xWO_3 , has been made for $0.22 \leq x \leq 0.60$. These measurements are consistent with earlier measurements for $x \geq 0.54$ which show that the electronic density of states at the Fermi level, $\rho(\epsilon_F)$, varies linearly with Na concentration instead of as $x^{1/3}$ as would be expected in the free-electron model. By making an analogy to band-structure calculations of the isostructural material ReO_3 , the linear dependence of $\rho(\epsilon_F)$ is found to be consistent with the nearly-free-electron model and with the ReO_3 band shape.

I. INTRODUCTION

The metal-insulator (*MI*) transition in the cubic sodium tungsten bronzes, Na_xWO_3 , was first noted in absorption-spectra measurements made by Brown and Banks¹ in 1954. Since then there have been many experiments in which both the nature of the transition at $x \cong 0.25$ and the physical properties of Na_xWO_3 were examined. Particularly intriguing was the observation by Greiner, Shanks, and Wallace² that the density of states at the Fermi energy $\rho(\epsilon_F)$, as determined from magnetic-susceptibility and specific-heat measurements³ for $x \geq 0.5$, does not follow the concentration dependence predicted by the nearly-free-electron model but varies linearly with Na concentration. The availability of cubic Na_xWO_3 crystals covering the concentration range $0.22 \leq x \leq 0.6$ has given us an opportunity to make measurements much closer to the *MI* transition. Measurements near the transition are essential if one is to have any hope of seeing special manifestations of the transition, such as enhancement of the specific heat or a departure from the linear dependence of $\rho(\epsilon_F)$ with Na concentration.

As a result of the extensive study of the *MI* transition in a number of materials during the past decade, it has become evident that the *MI* transition must be considered to result from several different effects. In the classic problem as proposed by Mott,⁴ one considered the long-range Coulomb interaction and correlations of electrons in an ordered solid as the atoms are brought close enough together to cause the transition from an insulator to a metal. In practice, however, it is a very difficult problem to expand or contract a lattice sufficiently by pressure to cause such a transition. Hence, other devices such as using doped semiconductors,⁵ compressed metallic gases,⁶ or systems where interatomic distances are changed with composition⁷ have been tried. This retreat from the ideal system introduces an ad-

ditional complication to the problem, in that the existence of a nonuniform potential may cause localization. Thus in any system in which disorder exists three mechanisms must be considered: electron-electron interactions as described by Mott⁴ and Hubbard,⁸ localization-delocalization in the Anderson sense,⁹ and percolation.⁵

Percolation has been previously used to describe the metal-semiconductor transition in heavily doped semiconductors. In this case it is assumed that a sphere of conductivity with a radius approximately equal to the Bohr radius of the charge carriers is associated with each impurity site. As the impurity concentration increases, more and more of the spheres overlap, forming clusters. Eventually as the clusters grow larger with increasing doping, they coalesce to form a conducting bridge across the crystal.

The sodium tungsten bronzes crystallize in the cubic perovskite structure for $0.48 \leq x \leq 0.95$ with the corner linked WO_6 octahedra at the corners of the unit cell forming a large interstitial position for the Na. Although for $x \leq 0.48$ Na_xWO_3 normally crystallizes in a tetragonal structure, Lightsey¹⁰ has been able to make crystals of the cubic phase with x as low as 0.22 by the process of diffusion dilution introduced by McNeill and Conroy.¹¹ Various earlier measurements indicate that the Na atom is completely ionized with the electron going into the $5d(t_{2g})$ orbitals of the tungsten.¹²

Sodium tungsten bronzes in the insulating state bear a striking resemblance to heavily doped *n*-type semiconductors in the semiconducting state. In both, one expects isolated ionized impurity atoms with electrons in extended orbits around them, and a transition to a metallic state as the impurity concentration is increased. Cubic Na_xWO_3 might be expected to be an ideal material for investigating the applicability of percolation theory to the *MI* transition since the x value for

the transition suggests that the bound electron is largely confined to a single lattice cell.

A percolation model has been used to interpret several previous experimental results on the metallic form of Na_xWO_3 . Electrical-resistivity measurements¹³ for $0.22 \leq x \leq 0.90$ have been fitted to a power-law relation predicted by Kirkpatrick¹⁴ using a resistor network version of a site percolation model. Also, Fuchs¹⁵ showed that the linear concentration dependence of $\rho(\epsilon_F)$ which we have noted is consistent with a percolation model.

II. EXPERIMENTAL PROCEDURES

The Na_xWO_3 samples used in this work were prepared by diffusing Na ions from thin slices of $\text{Na}_{0.60}\text{WO}_3$ that had been made by cathodic reduction of a tungsten oxide-sodium tungstate melt. This diffusion was done by annealing an appropriate mixture of the thin slices of $\text{Na}_{0.60}\text{WO}_3$, powdered $\text{Na}_{0.60}\text{WO}_3$, and WO_3 in an evacuated quartz tube until a uniform mixture of concentration x was achieved. In this way it was possible to prepare cubic Na_xWO_3 with Na concentrations as low as $x=0.22$. This technique is described in somewhat more detail in a forthcoming paper.¹⁶

Concentrations were determined by x-ray powder diffraction measurements of the unit cell dimension. Previous measurements¹⁷ had shown that Vegard's law was applied for $0.3 \leq x \leq 0.8$. Chemical analysis of a fraction of our samples indicated that Vegard's law is valid down to our lowest concentrations. Nonuniformity of the Na distribution was determined to be less than 20% by electron microprobe and x-ray line broadening. The samples were initially screened by discarding those which had nonuniform color, indicative of nonuniform sodium concentration, and those which showed anomalously high resistivity.

The calorimeter was essentially a copper can which could be maintained at a constant temperature (to within about $10 \mu\text{K}$) and could be evacuated or filled with exchange gas as required. The sample was mounted on a silicon chip platform $0.10 \times 0.20 \times 0.005$ in. which was attached to the sample container, which served as the heat sink, by 0.07-mm Mo-Re wire. The sample heater and sample thermometer were small 2-mg chips of a 0.1-W 100- Ω Allen-Bradley resistor epoxied to the underside of the silicon chip. The leads to the sample were made from the 0.07-mm Mo-Re wire which was superconducting during all the specific-heat measurements so that all heat could be assumed dissipated in the sample heater and so that a four-probe measurement of the resistance of the sample thermometer could be made

well away from the sample. The thermometers were calibrated against a calibrated Cryocal germanium resistance thermometer prior to each run, and all subsequent measurements were made without allowing the thermometers to be heated to greater than 10 K. The total thermal mass of the sample holder, heater, thermometer, and lead wires was less than 30% of the sample thermal mass in all cases.

Measurements were made by the time-honored technique of measuring the thermal time constant of the sample assembly as it relaxes back to the heat sink temperature. Typically decay constants ranged from 1 to 30 sec depending on sample sizes and the lengths of lead wire used.

Besides the basic simplicity of this technique in the measurement of small heat capacities, there are some advantages which are not readily apparent. First and possibly most important is the fact that one need only provide good temperature stability for times of approximately 10τ , 5τ to determine the equilibrium temperature and 5τ to measure τ . Another advantage is that as a result of the comparatively short time constant at liquid-He temperatures, it is possible to purge the sample of any adsorbed He gas that may have accumulated during cool down by heating the sample assembly to 15 K for a short period of time. Additionally, since the time constant measurement is basically a cooling process, one measures only the specific heat of the He gas itself and not an apparent specific heat caused by the heat of vaporization during a heat pulse.

Measurements were made on samples of mass ranging from 50 to 300 mg with Na concentrations of $0.22 \leq x \leq 0.60$. The samples were thermally linked to the sample holder with less than 1 mg of dilute GE 7031 varnish. The time constants were determined by a least-squares fit to the digitized data assuming an exponential decay. In no case was there a variance greater than 2% to the fitted data. No evidence of failure of the sample thermometer to track the sample was seen in any of the reported runs.

The specific-heat results were analyzed by attempting to fit the data to following relation:

$$C = \gamma T + \beta T^3, \quad (1)$$

where in the simple theory of metals γ is to be associated with the specific heat of the conduction electrons and β with that of the lattice. Figure 1 shows a plot of C/T vs T^2 for one of the samples as well as a least-squares fit to the data. The quality of fit shown here is typical of the measurements on all of the samples and of the measurements made on the empty sample holder. Table I summarizes the values of γ and β calculated for

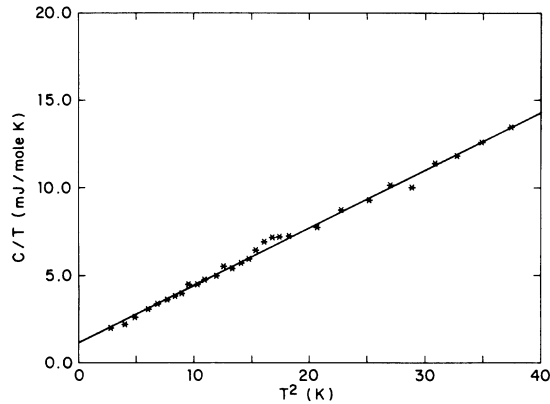


FIG. 1. Plot of C/T vs T^2 of $\text{Na}_{0.30}\text{WO}_3$. The solid line is the least-squares fit of $C/T = \gamma + \beta T^2$ to the data and *, the experimental results.

each sample after corrections had been made for the specific heat of the sample holder. Also shown in Table I are values of the Debye temperatures Θ_D , calculated from the following definition of Θ_D :

$$\beta = \frac{1}{5}(12\pi^4)n_f R(1/\Theta_D)^3, \quad (2)$$

where R is the gas constant and n_f the number of atoms per formula weight.

The magnetic susceptibility was measured using a commercially available Faraday balance at room temperature. Test runs at low temperature showed Curie-like paramagnetism below 25 K which was most likely due to unreacted sodium tungstate. Near room temperature, no temperature dependence of χ was measurable and it was assumed that the only contributions to the susceptibility came from the core diamagnetism χ_D , the Van Vleck paramagnetism χ_{VV} , and the paramagnetism due to the conduction electrons χ_e . Thus after any contributions to the measured χ from the quartz suspension were subtracted, the resultant χ could be assumed to be the sum of χ_D , χ_{VV} , and χ_e . In attempting to determine the magnitude of each of these terms, we can note that although the crystal structure of WO_3 is different from that of Na_xWO_3 , the basic unit of the struc-

ture in both cases is the corner linked WO_6 octahedron. In the case of the bronzes, however, Na^+ ions fill the large interstitial vacancies in the cubic perovskite structure. A reasonable determination of χ_e can thus be made by assuming that the contribution of the WO_3 lattice is essentially independent of Na concentration and that the Na is completely ionized. In this case, the measured susceptibility can be written

$$\chi = \chi_{\text{WO}_3} + x\chi_{\text{Na}^+} + \chi_e. \quad (3)$$

Thus χ_e can be calculated using the previously measured value of $\chi_{\text{WO}_3} = 13.9 \times 10^{-6}$ emu/mole² and $\chi_{\text{Na}^+} = -6.1 \times 10^{-6}$ emu/mole.¹⁸ The calculated room temperature values of χ_e are shown in Table I.

III. DISCUSSION

Wilson¹⁹ shows, to first approximation, that when exchange and correlation forces are ignored, the electronic specific-heat coefficient may be written

$$\gamma(x) = \frac{1}{3}\pi^2 k_B^2 \rho(\epsilon_F), \quad (4)$$

where k_B is Boltzman's constant. In the nearly-free-electron model

$$\rho(\epsilon_F) = (4m^*/h^2)(3\pi^2 x/a_0^3)^{1/3}, \quad (5)$$

where m^* is the reduced electron mass, h is Planck's constant, and a_0 is the dimension of the unit cell. From Eq. (5) we see that $\gamma(x)$ should be proportional to $x^{1/3}$. As seen in Fig. 2, this result is in conflict with the experimental values.

The susceptibility of the conduction electrons in the nearly-free-electron model is

$$\chi_e = \mu_B^2 \rho(\epsilon_F)(1 - m^2/3m^{*2}), \quad (6)$$

where μ_B is the Bohr magneton. Here again, using (5) and (6) we see in Fig. 3 that the predicted behavior disagrees with experimental measurements.

Clearly some explanation other than that of the nearly-free-electron model with a parabolic band

TABLE I. Summary of results.

Composition	γ (mJ/mole K ²)	β (mJ/mole K ⁴)	Θ_D (K)	χ_e (10^{-6} emu/mole)
$\text{Na}_{0.23}\text{WO}_3$	1.11	0.254	255	...
$\text{Na}_{0.24}\text{WO}_3$	0.93	0.360	284	5.3
$\text{Na}_{0.25}\text{WO}_3$	0.96	0.320	295	5.9
$\text{Na}_{0.27}\text{WO}_3$	0.90	0.276	311	5.4
$\text{Na}_{0.30}\text{WO}_3$	1.16	0.328	294	7.0
$\text{Na}_{0.33}\text{WO}_3$	7.2
$\text{Na}_{0.36}\text{WO}_3$	1.22	0.217	339	11.2
$\text{Na}_{0.60}\text{WO}_3$	1.89	0.170	375	18.6

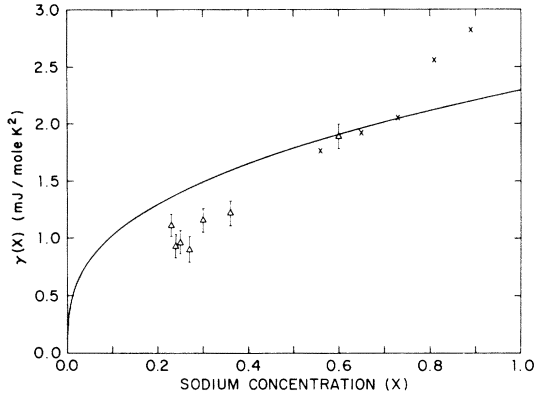


FIG. 2. Plot of $\gamma(x)$ vs concentration. The solid line is the concentration dependence predicted by the free-electron theory. Δ , results from present work. \times , results from Vest, Griffel, and Smith, Ref. 3.

is needed. To meet this need Fuchs¹⁵ proposed a percolation model that gave a linear relationship between $\rho(\epsilon_F)$ and x . In this model each unit cell in the crystal which contains a Na atom is considered to be an isolated particle of metal with its Fermi level the same as that of the idealized bulk material NaWO_3 . As the number of Na atoms increases and the isolated cells form clusters and eventually a spongy, nearly totally connected mass, the Fermi energy is assumed to remain constant with only the density of states at ϵ_F increasing linearly with the addition of each Na atom.

The prime motivation for this theory was that it did not seem reasonable to expect a band with

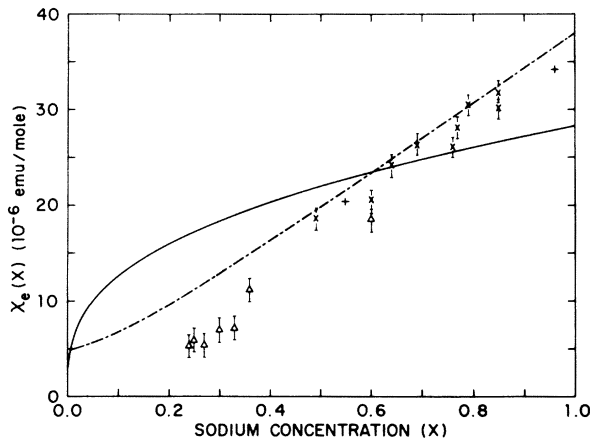


FIG. 3. Plot of $\chi_e(x)$ vs concentration. The solid line is the concentration dependence predicted by the free-electron theory. The dashed line is that calculated using $\rho(\epsilon) = Ae^{\epsilon/\epsilon_0}$ where A and ϵ_0 have been determined from the experimental values of $\gamma(x)$. Δ , results from present work. \times , results from Greiner, Shanks, and Wallace, Ref. 2. $+$, results from Kupka and Seinko, J. Chem. Phys. 18, 1296 (1950).

the functional dependence necessary to give $\rho(\epsilon_F)$ increasing linearly with x . Band theory calculations on the isostructural material ReO_3 , by Mattheiss,²⁰ however, show just such a dependence. The density of states curve calculated by Mattheiss can be fitted reasonably well by a relationship of the form $\rho(\epsilon) = Ae^{\epsilon/\epsilon_0}$, which gives the desired linear dependence to $\rho(\epsilon_F, x)$,²¹ i.e.,

$$\rho(\epsilon_F) = (x/\epsilon_0 a_0^3) + A. \quad (7)$$

Also in a calculation of the properties of a band in which the electron energy is a function of only two directions in k space, Wolfram²² shows that the density of states has an appropriate form to give a linear dependence to the specific heat. One should note that a band formed of these two-dimensional electron states could be a reasonable approximation for Na_xWO_3 since the electrons apparently fill the $5d(t_{2g})$ orbitals which are restricted to the faces of the unit cell.

It is interesting now to see how the coefficients A and ϵ_0 , determined from a least-squares fit of the specific-heat data using Fig. 2 compare with those determined by fitting the published data of Mattheiss of the adjusted band structure for ReO_3 . When this is done, one finds the remarkably good agreement shown in Table II.

Assuming that the previous discussion validates our approximation to the correct density of states, it is now possible to predict the susceptibility of the conduction electrons. χ_e can be represented by a sum of the Pauli-spin paramagnetism χ_p , and of a diamagnetic part χ_d . To first approximation, the spin paramagnetism can be written

$$\chi_p = \mu_B^2 \rho(\epsilon_F). \quad (8)$$

Wilson²³ shows that the most important contribution to the molar diamagnetism of the conduction electrons is

$$\chi_d = \frac{e^2 V}{12\pi \hbar^2 c^2} \int \left[\frac{\partial^2 \epsilon}{\partial k_x^2} \frac{\partial^2 \epsilon}{\partial k_y^2} - \left(\frac{\partial^2 \epsilon}{\partial k_x \partial k_y} \right)^2 \right] \frac{\partial f_0}{\partial \epsilon} d\vec{k}, \quad (9)$$

where the magnetic field is in the k_z direction and V is the molar volume, e the electronic charge, c the speed of light, and f_0 the Fermi distribution function. Assuming only that ϵ is a function of $|k|$, it is possible to show that to zeroth order in kT/ϵ_F ,

TABLE II. Comparison of band parameters for ReO_3 and Na_xWO_3 .

	A (states/eV cm ³)	ϵ_0 (eV)
ReO_3	0.24×10^{22}	1.26
Na_xWO_3	0.26×10^{22}	0.92

$$\chi_d = \frac{-e^2 V}{9\hbar^2 c^2} \left(2 \frac{d\epsilon}{dk} + k \frac{d^2\epsilon}{dk^2} \right)_{\epsilon_F} \quad (10)$$

It is easy to show that for a band with a density of states given by $\rho(\epsilon) = A e^{\epsilon/\epsilon_0}$ that

$$\epsilon(k) = \epsilon_0 \ln[(k^3/3\pi^2 A \epsilon_0) + 1]. \quad (11)$$

χ_e can now be calculated using (8), (9), (10), and (11) where k_F is related to x by

$$n = x/a_0^3 = k_F^3/3\pi^2. \quad (12)$$

The results of this calculation are compared with the experimental results in Fig. 3. The fit, while not exact, is considerably better than that obtained using the free-electron model. Primarily this is due to the fact that by using the density of states given in Eq. (11), m^* is now dependent on the band filling. It would be a little surprising if the agreement were much better since in deriving (10), an assumption was made that k was isotropic, whereas the Wolfram calculation implies a strong anisotropy. It is also possible that the increasing departure from the predicted behavior at small x is some, as yet unexplained, effect of the *MI* transition.

It should be noted that the model described here makes several simplifying assumptions which might affect the results. Possible effects on χ of changes in the electron-phonon coupling are ignored as is the possibility of any Coulomb enhancement of χ . Also, χ_{VV} is assumed to be concentration independent.

IV. CONCLUSIONS

One is now left with the necessity of reconciling the two models. As noted before, the percolation model gives a good approximate value for the critical concentration, a good fit to the resistivity results, and also yields the linear dependence of $\rho(\epsilon_F)$ vs x . However, it seems unlikely to be valid at high Na concentration when every cell

must be considered part of the bulk material. Recent work supports such skepticism. X-ray photoemission measurements²⁴ indicate that there is a uniform electron density at the *W* sites, and that there is a well defined conduction band with the number of states increasing with increasing concentration. In addition, Tunstall²¹ shows that the x dependence of NMR relaxation times is inconsistent with extension of the percolation model to values of x substantially above the *MI* transition at $x \cong 0.25$.

It would seem that a reasonable explanation of what is happening would be a combination of both models. In a range near the transition, a percolation model should be a reasonable approximation. The model should be able to predict the critical concentration and perhaps the initial form of the resistivity versus concentration results. However, as the electron concentration increases substantially above that of the *MI* transition, the metallic clusters are fully overlapped and percolation ideas lose their utility. Although percolation theory with the electron fully restricted to a single lattice cell does predict the correct concentration dependence of $\rho(\epsilon_F)$ and of the resistivity over the full range of x , these results appear to be coincidental. A far more useful model and one that is consistent with all experimental measurements is one in which added electrons fill a rigid nonparabolic band of the shape predicted by band structure calculations.

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* Present address: Central Research and Development Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. 19898.

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