Schmidt and Keesom<sup>6</sup> in 1937. Although this equation was designed to fit the experimental results only in the range from 2.2°K to 4.3°K, it is interesting to extrapolate it from 4.3°K to 5°K. This extrapolation is given as curve *B* in Fig. 1. It may be seen that below 4.8°K the extrapolated curve of Keesom and Lignac (*B*) is in

<sup>6</sup>G. Schmidt and W. H. Keesom, Physica 4, 971 (1937).

better agreement with the carbon thermometer data than the curve of van Dijk and Shoenberg (A). It would appear that a redetermination of the vapor pressure curve between  $4.2^{\circ}$ K and the critical point is desirable.

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# Electrical Resistivity and Hall Coefficient of Sodium Tungsten Bronze\*

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The electrical resistivity and Hall coefficient of single crystals of sodium tungsten bronze  $(Na_xWO_s)$  have been measured as a function of temperature and as a function of sodium concentration. The resistivity decreased linearly with decreasing temperature from 300°K to 125°K and was very nearly constant below 30°K. The resistivity at 26°C exhibited a minimum value of  $(3.20\pm0.14)$  (10<sup>-5</sup>) ohm-cm at  $x\cong0.75$ . The residual resistivity at 0°K also exhibited a minimum at  $x\cong0.75$  and had a value of  $(1.25\pm0.10)$  (10<sup>-5</sup>) ohmcm. The variation of the Hall coefficient with temperature was less than 2 percent over the temperature range 78°K to 370°K. The Hall coefficient varied inversely with the sodium concentration from x=0.584to x=0.897, and over this entire concentration range the Hall coefficient corresponded to one free electron for each sodium atom in the crystal. Hence, the anomalous minimum in the resistivity at  $x\cong0.75$  must be attributed solely to an anomalous maximum in the electron mobility. An adequate explanation of the minimum in resistivity does not seem possible in terms of thermal scattering alone.

#### I. INTRODUCTION

**C**ODIUM tungsten bronze is the nonstoichiometric  $\mathbf{J}$  compound Na<sub>x</sub>WO<sub>3</sub>, where x lies between zero and one. Huibregtse, Barker, and Danielson<sup>1</sup> measured the electrical resistivity and Hall coefficient of single crystals of sodium tungsten bronze having x=0.66. They found the resistivity to increase linearly with increasing temperature in the temperature range  $-160^{\circ}$ C to 20°C, and obtained a Hall coefficient which corresponded to one conduction electron for each sodium atom in the crystal. Brown and Banks<sup>2</sup> measured the resistivity of single crystals as a function of sodium concentration (0.527 < x < 0.852) and as a function of temperature ( $-160^{\circ}C < T < 360^{\circ}C$ ). Their results not only confirmed the metallic nature of the conductivity but showed that both the resistivity and the slope of the resistivity-temperature curve exhibited a minimum at a sodium concentration corresponding to x=0.70. To explain this minimum in the resistivity, they tentatively proposed an equilibrium between undissociated sodium atoms and sodium ions plus free electrons. For sodium concentrations below x=0.70, they suggested that each sodium atom might introduce into the crystal one free electron and one random scattering center (Na<sup>+</sup>); while above x=0.70, the addition of undissociated sodium atoms might contribute only additional scattering centers. The increased resistivity as x decreases below 0.70 could be caused by a decrease in the number of free electrons, while the increase in in resistivity about 0.70 could be caused by an increase in the number of scattering centers.

The present investigation was undertaken to test this hypothesis by determining the Hall coefficient, and hence the concentration of free electrons as a function of sodium concentration. By extending both resistivity and Hall data it was hoped that a better theoretical understanding of the anomalous minimum in resistivity at x=0.70 could be obtained.

## **II. SODIUM CONCENTRATION**

The sodium tungsten bronze crystals used in these experiments were grown by a method described by Brimm, Brantley, Lorenz, and Jellinek.<sup>3</sup> Sodium tungstate, tungstic oxide, and tungsten were heated in a porcelain crucible to 1000°C for six hours and slowly cooled to 700°C. The best and largest crystals were formed when the mole ratio of Na<sub>2</sub>WO<sub>4</sub>:WO<sub>3</sub>:W was about 6.4:4:1. Such crystals had a sodium concentration corresponding to  $x \cong 0.75$  and often had crystal faces larger than 5 mm by 5 mm. The sodium concent

<sup>\*</sup> Contribution No. 275 from the Institute for Atomic Research and Department of Physics, Iowa State College, Ames, Iowa Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

<sup>&</sup>lt;sup>1</sup> How at the U. S. Salinity Laboratory, Riverside, California. <sup>1</sup> Huibregtse, Barker, and Danielson, Phys. Rev. 84, 142 (1951).

<sup>&</sup>lt;sup>1</sup> Hubregtse, Barker, and Danielson, Phys. Rev. 84, 142 (1951) <sup>2</sup> B. W. Brown and E. Banks, Phys. Rev. 84, 609 (1951).

<sup>&</sup>lt;sup>3</sup>Brimm, Brantley, Lorenz, and Jellinek, J. Am. Chem. Soc. 73, 5427 (1951).

tration was increased or decreased by increasing or decreasing the proportion of sodium tungstate in the initial mixture. The crystals were cleaved easily along (100) planes into rectangular parallelepipeds about 3 mm in length and 2 mm in width and 1 mm in thickness.

The cubic perovskite structure of the bronzes was first suggested by de Jong.<sup>4</sup> Hägg<sup>5</sup> and Straumanis<sup>6</sup> have shown that the structure is cubic only when 0.3 < x < 1.0 and that the lattice constant  $a_0$  increases as x increases. This change of lattice constant with xis the most convenient and reliable method for measuring the sodium concentration.

In order to determine the lattice constant with precision, the following procedure was used. A portion of each crystal upon which electrical measurements were made was powdered and an x-ray powder pattern taken. The interplanar spacings for the eight diffraction lines having the largest Bragg angles were used to obtain eight values for the lattice constant. These eight values for  $a_0$  were plotted as a function of  $\frac{1}{2} \left[ (\cos^2\theta / \sin\theta) \right]$  $+(\cos^2\theta/\theta)$ ], where  $\theta$  is the Bragg angle. This function has been proposed by Nelson and Riley.<sup>7</sup> The value of  $a_0$  extrapolated to  $\theta = 90^\circ$  was taken as the precise lattice constant.

The following equation relating the lattice constant  $a_0$  in angstroms to the sodium concentration x was used:

$$a_0 = (a_1 x + a_2),$$
 (1)

where  $a_1 = 0.0820$  and  $a_2 = 3.7845$ . This linear relationship has been established by three independent investigations.<sup>3,6,8</sup> However, there is some disagreement in the value of  $a_0$  for x=1. In this investigation we have taken 3.8587 kx units=3.8665A as the value for  $a_0$ when x=1. This is the value given by Banks<sup>8</sup> and appears to be the most reliable.

The sodium concentration in atoms per cubic centimeter is

$$(x/a_0^3)10^{24} = [(12.20a_0 - 46.15)/a_0^3]10^{24}, \qquad (2)$$

where  $a_0$  is expressed in angstroms.

The x-ray patterns revealed the presence of free metallic tungsten in many of the crystals. Brimm et al.3 also reported the presence of tungsten which they were unable to eliminate from the crystals. This free metallic tungsten probably results from the tendency of the crystals to grow around any small particles of tungsten which fail to react completely. If one uses tungsten wires instead of tungsten powder in the reaction, Sidles<sup>9</sup> has found that all the crystals grow on the tungsten wires. The existence of small amounts of free tungsten in the crystals appeared to have no appreciable effect on the electrical resistivities or Hall coefficients of the crystals.

## **III. ELECTRICAL RESISTIVITY**

Resistivity measurements were made with a dc potential method in the temperature range 10°K to 300°K. A Collins helium cryostat was used to obtain the low temperatures. The sample holder consisted of two small brass blocks mounted on a Bakelite base. These blocks served as the current electrodes and were faced with indium solder to give good electrical contact and firm mechanical support. One of the electrodes was stationary and the other could be forced tightly against the sample by means of a screw adjustment. Pressure was necessary to give good electrical contact, but care was necessary in applying pressure because the crystals fractured rather easily. The detecting probes were 0.020-inch tungsten wires pointed on the end by dipping in molten potassium nitrite. The probes were springloaded to insure good contact with the crystal. Owing to the smooth, hard faces of the crystals, the probes had some tendency to shift position if not held firmly in place by spring loading. The potential between the probes was measured with a Brown precision indicator. The sample current was about one ampere and was determined by measuring the potential across a 0.001-ohm precision resistor. The temperature was measured by means of two copper-constantan thermocouples in thermal contact with the current electrodes and about 1 cm from the samples. The thermocouple voltages were read on a Rubicon Type K potentiometer. The thermocouples had previously been calibrated against a platinum resistance thermometer down to 10°K. Potential differences between the probes were measured for both positive and negative directions of the sample current and for different values of the current. These potential differences were always found to be linear with current. Since the resistance of the samples was of the order of a few milliohms, the voltage measured, when the sample current was one ampere, was of the order of a few millivolts.

The results of the resistivity measurements are shown in Fig. 1.<sup>10</sup> The resistivity was found to decrease linearly with decreasing temperature from 300°K to about 125°K. Below 30°K the resistivity changed very little with temperature. By extrapolating to absolute zero the residual resistivities were obtained. In Fig. 2 the residual resistivity and the room-temperature resistivity are each plotted as a function of sodium concentration. The residual resistivity was subtracted from the total room-temperature resistivity to obtain the temperature-dependent resistivity, which is represented by the dashed line in the figure. It is seen that the residual resistivity has almost half the room-temperature value of the resistivity. Owing to this high residual resistivity, it was not possible to verify the

<sup>&</sup>lt;sup>4</sup> W. F. de Jong, Z. Krist. 81, 314 (1932). <sup>5</sup> G. Z. Hägg, Nature 135, 874 (1935).

<sup>&</sup>lt;sup>6</sup> M. E. Straumanis, J. Am. Chem. Soc. 71, 679 (1949). <sup>7</sup> J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) 57,

<sup>160 (1945)</sup> 

 <sup>&</sup>lt;sup>8</sup> E. Banks, 3rd Interim Report on Lattice, Polytechnic Institute of Brooklyn, Brooklyn, New York (July 6, 1951), Multigraphed.
<sup>9</sup> P. H. Sidles, Iowa State College, private communication.

<sup>&</sup>lt;sup>10</sup> Detailed data is available in the unclassified U. S. Atomic Energy Commission Report ISC-350 (unpublished).



FIG. 1. Resistivity of  $Na_xWO_3$  as a function of temperature.

dependence of the resistivity upon temperature at low temperatures  $(\rho \sim T^5)$  with the sensitivity of the equipment available.

The resistivity at 26°C exhibited a minimum value of  $(3.20\pm0.14)$   $(10^{-5})$  ohm-cm at  $x\cong0.75$ , in good agreement with the results of Brown and Banks.<sup>2</sup> The resistivity at 26°C was  $(12.5\pm0.23)$   $(10^{-5})$  ohm-cm at x=0.584, and  $(5.89\pm0.20)$   $(10^{-5})$  ohm-cm at x=0.863. The residual resistivity at 0°K also exhibited a minimum value. The minimum in the residual resistivity had a value of  $(1.25\pm0.10)$   $(10^{-5})$  ohm-cm at  $x\cong0.75$ .



FIG. 2. Resistivity of  $Na_xWO_3$  as a function of sodium concentration. Curve A is the measured resistivity at  $T=299^{\circ}K$ , curve B is the extrapolated residual resistivity at  $T=0^{\circ}K$ , and curve C=A-B is the temperature-dependent part of the resistivity at  $T=299^{\circ}K$ .

#### IV. HALL COEFFICIENT

The Hall coefficient was measured using an alternating current method similar to that described by Huibregtse *et al.*<sup>1</sup> Figure 3 is a block diagram of the circuit. An electronic oscillator-power amplifier delivered to the sample about 3 amperes of 100-cycle alternating current through an imepdance-matching transformer. The Hall voltage  $(V_H)$  was first amplified by a narrow-band amplifier, which had a voltage gain of about  $8.5(10^6)$ , and then measured on a vacuumtube voltmeter. Resistor  $R_1$ , which was placed in series with the sample in order to measure the primary current, had a value of 0.00116 ohm. A voltage divider paralleling this resistor  $R_1$  reduced the voltage by a factor of

 $R_3/(R_2+R_3) = 0.107/(1000+0.107) = 1.07(10^{-4}).$  (3)

In this way the voltage proportional to the primary current was reduced to the same order of magnitude as the Hall voltage. This reduced voltage  $V_3$  across the resistor  $R_3$  was amplified and measured in the same manner as the Hall voltage. Since only the ratio of the Hall voltage to the sample current appears in the expression for the Hall coefficient, only the above voltagedivider ratio and not the gain of the amplifier need be known. The current supply also provided a voltage of variable phase and amplitude to the Hall voltage measuring circuit. This voltage was used to buck out any voltage that might be present at zero magnetic field due to misalignment of the Hall probes and to inductive pickup. If the Hall voltage and a voltage in phase with the current are fed through an electronic switch onto an oscilloscope, and the phase of the two voltages compared, the negative sign of the Hall coefficient can be demonstrated, as pointed out by Huibregtse et al.1

The sample holder was similar to that used for the resistivity measurements. The sample was held firmly between two brass electrodes faced with indium solder. The movable electrode was screwed as tightly against the sample as was possible without breaking the crystal. The two Hall probes were pointed 0.020-inch tungsten wires and were spring-loaded. The sample holder was braced securely between the pole pieces of the magnet to prevent vibration, and all cables were shielded to minimize inductive pickup. Magnetic fields up to 10 000 oersteds were supplied by a Consolidated electromagnet, model 23-104A.

Several values of the Hall voltage for each direction of the magnetic field were averaged to obtain the value used in each calculation. The observed Hall voltage varied linearly with both primary current and magnetic field. Several separate determinations of the Hall coefficient were made for each crystal, and the average was calculated. The signal-to-noise ratio was usually over forty to one. In order to measure the Hall coefficient at low temperatures, the sample and holder were inserted into a Dewar which was filled with liquid nitrogen and which was placed between the poles of the magnet. A small furnace was constructed for measurements above room temperature. The highest temperature used was 96°C, since above this temperature the indium solder began to soften and vibration of the sample took place when the magnetic field was applied. The Hall coefficient varied less than 2 percent with temperature in the temperature range -196°C to 96°C. This variation was less than the precision of the measurements. Hence, within our experimental error, the Hall coefficient appeared to be independent of temperature from -196°C to 96°C.

The Hall coefficient  $(R_H)$  is given by the equation

$$R_H = (10^8 V_H t / IHf) \text{ cm}^3/\text{coulomb}, \qquad (4)$$

where  $V_H$  is the Hall voltage in volts, t is the sample thickness in centimeters, I is the current through the sample in amperes, and H is the magnetic field in oersteds. The shape correction factor (f) was necessary because the length of the sample was always less than four times the width. Appropriate correction factors for various length-to-width ratios are given by Volger.<sup>11</sup>

The sample current is seen from Eq. (3) to be given by the voltage  $V_3$  across the resistor  $R_3$ :

$$I = V_3(R_2 + R_3) / R_1 R_3 = V_3 / (12.4) (10^{-8}).$$
 (5)

Hence from Eq. (4) the Hall coefficient is

$$R_H = (V_H/V_3)(12.4 t/Hf) \text{ cm}^3/\text{coulomb.}$$
 (6)

The ratio  $(V_H/V_3)$  was obtained from the experimentally measured voltages  $gV_H$  and  $gV_3$ , where g is the gain of the amplifier.

The results of our measurements are given in Table I. The value for the Hall coefficient at x=0.658 is in good agreement with the results of Huibregtse *et al.*<sup>1</sup> They reported  $-(5.1\pm0.2)(10^{-4})$  cm<sup>3</sup>/coulomb compared to an average value of  $-(5.31\pm0.17)(10^{-4})$  cm<sup>3</sup>/coulomb for this investigation.

The electron density (n) corresponding to each value of the Hall coefficient in Table I was calculated from the free-electron relation  $R_H = -1/ne$ , where e is the magnitude of the electronic charge. The lattice constant in angstroms and the sodium concentration in atoms per cubic centimeter corresponding to each value of xin Table I were calculated from the empirical equations (1) and (2). The electron density is plotted as a function of sodium concentration in Fig. 4. The estimated probable error, which arises from uncertainty in the Hall coefficient measurements, is also indicated. Within experimental error, the experimental points for all sodium concentrations fall on a line which has a slope of 45 degrees and which represents one free electron for each sodium atom in the crystal. The free-electron concentration and the sodium concentration thus appear



FIG. 3. Block diagram of Hall equipment.

to be equal over the entire range of sodium concentration.

Hence, the anomalous minimum in the resistivity at x=0.75 must be attributed solely to an anomalous maximum in the electron mobility. The electron mobility ( $\mu$ ) was calculated from the Hall coefficient ( $R_H$ ) and the resistivity ( $\rho$ ) by the equation  $\mu = R_H/\rho$ . The values substituted for the Hall coefficients corresponded to one free electron per sodium atom, and the values

TABLE I. Hall coefficients for sodium tungsten bronze  $(Na_xWO_3)$ .

Sample number	x	t (cm)	gV <sub>H</sub> (volts)	gVs (volts)	H (oersteds)	f	$\begin{array}{c} -R_H(104) \\ (\text{cm}^3/ \\ \text{coulomb}) \end{array}$
1	0.584	0.154	6.15	4.44	5250	0.826	6.10
2	0.643	0.185	4.28	3.62	5250	0.910	5.68
3	0.658	0.135	2.76 6.06 8.98 4.39	3.96 4.07 4.30 2.00	2580 5250 6900 8580	0.875 0.875 0.875 0.875 0.875	5.20 5.45 5.70 4.93
4	0.705	0.154	7.77	3.72	8580	0.890	5.22
5	0.729	0.143	5.30	2.39	8580	0.955	4.87
6	0.743	0.121 0.105	4.95 5.83	1.92 1.88	8580 8580	0.967 0.975	4.70 4.87
7	0.758	0.103	7.70	2.50	8580	0.963	4.80
8	0.796	0.114	2.39	3.36	2580	0.930	4.20
9	0.800	0.110	7.60 4.89 7.10 8.73	3.18 2.30 2.91 3.25	7600 7830 8580 8580	0.942 0.920 0.920 0.920	4.53 4.04 4.22 4.64
10	0.844	0.120	2.25 2.10 1.83 4.75	3.58 3.31 2.97 3.68	2580 2580 2580 5250	0.830 0.830 0.830 0.830	4.38 4.41 4.28 4.42
11	0.851	0.141 0.099	1.30 3.16	2.20 1.89	2580 5250	0.990 0.968	4.03 4.08
12	0.864	0.130	5.02 7.20	3.82 3.95	2580 6900	0.995 0.995	$\begin{array}{c} 4.04 \\ 4.28 \end{array}$
13	0.897	0.116	$1.90 \\ 1.68 \\ 1.64 \\ 1.38$	3.25 2.86 2.85 2.41	2580 2580 2580 2580	0.795 0.795 0.795 0.795	$\begin{array}{c} 4.11 \\ 4.12 \\ 4.02 \\ 4.02 \end{array}$

<sup>&</sup>lt;sup>11</sup> J. Volger, Phys. Rev. 79, 1023 (1950).



FIG. 4. The electron density of Na<sub>x</sub>WO<sub>3</sub> as a function of sodium concentration. These two quantities are observed to be equal in absolute magnitude from x=0.58 to x=0.90.

substituted for the resistivity were taken from the experimental resistivity curves. In Fig. 5 the mobility of the electrons at 0°K and at 273°K is plotted as a function of sodium concentration. Each curve exhibits a maximum at  $x \cong 0.75$ .

## **V. ANOMALOUS MINIMUM IN RESISTIVITY**

The anomalous minimum in the resistivity of  $Na_xWO_3$ , when the resistivity is plotted as a function of x, has been the subject of much speculation ever since its discovery by Brown and Banks.<sup>2</sup> These authors suggested a tenative hypothesis based upon an equilibrium between dissociated and undissociated sodium atoms at x=0.70. At this concentration, the number of



FIG. 5. The mobility of the electrons in  $Na_xWO_3$  as a function of sodium concentration.

charge carriers would remain constant, but the number of scattering centers would continue to increase as xexceeded 0.70. Thus, the resistivity would decrease up to x=0.70 because of the increase in the number of charge carriers, and would increase for x > 0.70 because of the increase in the number of scattering centers. However, Fig. 4 shows that the Hall coefficient has a value corresponding to one free electron for each sodium atom over the entire concentration range (0.58 < x < 0.90). Hence, no explanation which involves an anomalous behavior in the total number of charge carriers appears to be tenable.

Juretschke<sup>12</sup> has proposed a correlation between a possible minimum in the resistivity-pressure curve of pure sodium and the minimum in the resistivity-sodium concentration curve of Na<sub>x</sub>WO<sub>3</sub>. Bridgman<sup>13</sup> originally predicted a resistivity minimum for pure sodium at a pressure of 24 000 kg/cm<sup>2</sup>. Later, he found a broad minimum at about 45 000 kg/cm<sup>2</sup>. The calculations of Bardeen<sup>14</sup> do not show any minimum up to a pressure of 30 000 kg/cm<sup>2</sup>. The arguments of Juretschke are based upon a correlation of the atomic volume in sodium with that in  $Na_xWO_3$ . Although the change in resistance with atomic volume is in the right direction to produce a minimum, the magnitude of the effect seems to be too small to account for the observed minimum. This may be seen from the following considerations.

According to Bloch<sup>15</sup> and Bethe<sup>16</sup> the resistivity  $(\rho)$ of a metal, due to interaction of the electrons with the lattice vibrations, is given by

$$\frac{1}{\rho} = \frac{ne^{2}l}{hK} = \frac{8Me^{2}k}{h^{3}C^{2}} n_{0} \left[ K \left( \frac{d\epsilon}{dK} \right)^{2} \right]_{\epsilon=\xi} \Theta^{2} \frac{1}{T}, \quad (7)$$

where n is the number of electrons per cm<sup>3</sup>, e is the magnitude of the charge of an electron, l is the mean free path, K is the propagation vector whose magnitude is  $2\pi/\lambda = P/\hbar$  where  $\lambda$  is the de Broglie wavelength and P is the crystal momentum, M is the mass of an atom, k is Boltzmann's constant,  $h = 2\pi\hbar$  is Planck's constant, C is the interaction constant between the electrons and the lattice vibrations,  $n_0$  is the number of electrons per atom,  $\zeta$  is the energy  $\epsilon$  of an electron at the Fermi level,  $\Theta$  is the Debye temperature, and T is the absolute temperature.

We can with some confidence apply free-electron theory to both sodium and Na<sub>x</sub>WO<sub>3</sub>. Hence, we assume

$$\epsilon = (\alpha \hbar^2 / 2m) K^2, \tag{8}$$

<sup>12</sup> H. J. Juretschke, Phys. Rev. 86, 124 (1952).
<sup>13</sup> P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, London, 1949), pp. 283 and 430; Proc. Am. Acad. Arts Sci. 72, 157 (1937); 81, 165 (1952).
<sup>14</sup> J. Bardeen, J. Appl. Phys. 11, 88 (1940), see Fig. 13.
<sup>15</sup> F. Bloch, Z. Physik 52, 555 (1928).
<sup>16</sup> A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Springer, Berlin 1933) Vol 24 No. 2 p. 523

Berlin, 1933), Vol. 24, No. 2, p. 523.

where  $m/\alpha$  is the effective mass of the conduction electrons. Also, the Fermi energy  $\zeta$  is given by

ζ=

$$(\alpha h^2/2m)(3n/8\pi)^{\frac{2}{3}}.$$
 (9)

Hence,

$$\begin{bmatrix} K(d\epsilon/dK)^2 \end{bmatrix}_{\epsilon=\sharp} = (\alpha\hbar^2/m)^2 (2m\xi/\alpha\hbar^2)^{\frac{3}{2}} = 3(\alpha\pi\hbar^2/m)^2(n_0/\Omega), \quad (10)$$

where  $\Omega = n_0/n$  is the volume occupied by one sodium atom. For pure sodium or for Na<sub>x</sub>WO<sub>3</sub>,  $n_0 = 1$ , and  $\Omega$ is reciprocal of electron density.

The interaction constant C for sodium is given by Peterson and Nordheim<sup>17</sup> and by Bardeen<sup>18</sup> by the equation

$$C = b\zeta, \tag{11}$$

where the constant b=0.84, and the Fermi energy  $\zeta$  is given by Eq. (9).<sup>19</sup>

Substituting (10) and (11) in (7) we obtain for the resistivity,

$$1/\rho = B\Omega^{\frac{1}{2}}\Theta^2(1/T), \qquad (12)$$

where the constant

$$B = (4kMe^2/\pi^4\hbar^3b^2)(\pi n_0^2/3)^{\frac{1}{3}}.$$
 (13)

It is thus seen that the room-temperature resistivity of pure sodium or  $Na_xWO_3$ , due to interaction of the electrons with the lattice vibrations, depends upon  $\Omega$ , the volume occupied by one sodium atom, and upon  $\Theta$ , the Debye temperature.

As the pressure on the sodium metal is increased, Gruneisen<sup>20</sup> has suggested that the Debye temperature will be increased and that the increase will correspond to an increase in the forces between atoms and, hence, in the maximum frequency of the lattice vibrations. Also, the volume occupied by each sodium atom will clearly be decreased. The decrease in resistivity owing to this increase in  $\Theta$  predominates over the small increase in resistivity owing to the decrease in  $\Omega$ , and hence the resistivity of sodium decreases with increasing pressure.

<sup>18</sup> J. Bardeen, Phys. Rev. 52, 688 (1937).

<sup>19</sup> This dependence of C upon  $\xi$  was not considered by N. H. Frank, Phys. Rev. 47, 282 (1935). <sup>20</sup> E. Gruneisen, Verhandl. deut. physik. Ges. 15, 186 (1913).

For  $Na_xWO_3$  it follows from Eqs. (2) and (1) that the volume occupied by each sodium atom, (i.e., reciprocal of electron density) is given by

$$\Omega = a_0^3 / x = a_2^3 / x, \tag{14}$$

if we assume that the entire volume of the crystal is available to the free electrons. If the volume occupied by the oxygen and tungsten atoms is excluded, Juretschke<sup>12</sup> gives for the volume occupied by each sodium atom

$$\Omega = (19.6/x + 2.9) A^3. \tag{15}$$

In either case, the resistivity increases only as the cube root of the concentration x.

It appears reasonable to attribute the initial decrease in resistivity to an increase in the Debye temperature. However, even if we assume that the Debve temperature becomes constant at x=0.75, the increase in resistivity cannot be explained quantitatively by the increase in x. As x increases from x=0.75 to x=0.85. Fig. 2 shows that the temperature-dependent part of the resistivity increases from  $2(10^{-5})$  ohm-cm to 3.4(10<sup>-5</sup>) ohm-cm, or 70 percent. The decrease in  $\Omega^{\frac{1}{3}}$ from either Eq. (14) or (15) is only 4 percent. Thus, it appears that the change in atomic volume of the sodium is much too small to account for the observed minimum in the resistivity-concentration curve.

In addition to the above argument, the observed minimum in the residual resistivity of  $Na_xWO_3$  at  $T=0^{\circ}$ K requires some explanation apart from the properties of pure sodium which would have very little residual resistivity.

A conceivable explanation of the minimum in resistivity might be made in terms of ordering of the sodium atoms at  $x \cong 0.75$ . So far, however, we have not found any evidence for such ordering from a preliminary examination of x-ray powder patterns. Also, the minimum in resistivity is possibly not as sharp as one might expect in an ordering phenomenon. However, a further search for ordering should be made.

#### ACKNOWLEDGMENT

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<sup>&</sup>lt;sup>17</sup> E. L. Peterson and L. W. Nordheim, Phys. Rev. 51, 355 (1937).