

$R'$  bands, never exceeded the maximum value attained as a result of the initial irradiation at RT. Furthermore, without bleaching this  $M'$  band following the irradiation at RT, there was no significant change in it as a result of a reirradiation at LNT, although the crystal contained  $M^+$  centers. The concentration of  $M'$  centers apparently attains a maximum value as a result of the initial irradiation at RT. It is possible, however, that during the initial irradiation at RT,  $M^+$  centers,

analogous to the case of  $R^+$  centers, transform mostly to  $M$  centers but also partially to  $M'$  centers.

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## Effects of Ordering on the Transport Properties of Sodium Tungsten Bronze\*

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The electrical resistivities, Hall coefficients, and Seebeck coefficients of metallic  $\text{Na}_x\text{WO}_3$  have been measured as functions of the sodium concentration ( $x$  value) from  $x=0.4$  to  $x=0.9$  and also a function of the temperature from 4 to 300°K. The resistivity, Hall coefficient, and Seebeck coefficient each showed an anomaly at  $x=0.75$  where the sodium atoms are ordered. These results are the first demonstration of ordering effects in any transport property of any tungsten bronze. A careful selection of crystals that were homogeneous in electrical resistivity was necessary in order to see these ordering effects. For homogeneous crystals, the Hall coefficients were different from those previously reported and do not predict the exact number of free electrons.

### INTRODUCTION

THE nonstoichiometric compounds  $M_x\text{WO}_3$  (where  $M$  represents an alkali metal) are commonly referred to as the alkali tungsten bronzes, and, since their discovery,<sup>1</sup> their properties have stimulated the interest of many investigators. Although other bronzes have been prepared and investigated, the alkali tungsten bronzes have received the most attention. In particular, extensive data exist on sodium tungsten bronze,  $\text{Na}_x\text{WO}_3$ .

The resistivity data<sup>2-5</sup> of cubic  $\text{Na}_x\text{WO}_3$  ( $1.0 > x > 0.48$ ), together with the Hall coefficients,<sup>5</sup> indicated that cubic  $\text{Na}_x\text{WO}_3$  exhibited metallic behavior and that each sodium atom contributes one electron to the conduction band. However, the resistivity which was measured by Brown and Banks<sup>4</sup> and by Gardner and Danielson<sup>5</sup> showed a definite minimum in the resistivity versus the sodium concentration at  $x=0.75$ . Brown and Banks interpreted the minimum in the resistivity in

terms of an equilibrium between the undissociated sodium atoms and the sodium ions plus free electrons, while Gardner and Danielson suggested that the minimum was due to the ordering of the sodium atoms. However, Ellerbeck *et al.*<sup>6</sup> showed that the minimum in the resistivity was due to the inhomogeneous crystals which were used by the previous investigators and that when homogeneous single crystals were used for measurements, there was no minimum in the resistivity-versus-sodium-concentration curve. In fact, Ellerbeck *et al.* found no evidence of any anomaly at  $x=0.75$  even though partial ordering of the sodium atoms had been seen at  $x=0.75$  by Atoji and Rundle<sup>7</sup> in their neutron-diffraction work. However, Mackintosh<sup>8</sup> pointed out that the experimental evidence did not necessarily rule out the possibility of a maximum in the conductivity at  $x=0.75$  and suggested that further measurements be made in the region of the superlattice structure.

Thus, in regard to the electrical properties of  $\text{Na}_x\text{WO}_3$ , there still exist two important questions. First, if greater care were taken in the preparation of the  $\text{Na}_x\text{WO}_3$  single crystals and if more samples were used near the region of the superlattice structure, would it be possible to detect in the electrical transport prop-

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† U. S. Atomic Energy Commission Postdoctoral Fellow.

<sup>1</sup> F. Wholer, *Ann. Physik Chem.* **2**, 345 (1824).

<sup>2</sup> M. D. Straumanis and W. Dravnieks, *J. Am. Chem. Soc.* **71**, 683 (1949).

<sup>3</sup> E. J. Huibregtse, D. B. Barker, and G. C. Danielson, *Phys. Rev.* **84**, 142 (1951).

<sup>4</sup> B. W. Brown and E. Banks, *Phys. Rev.* **84**, 609 (1951).

<sup>5</sup> W. R. Gardner and G. C. Danielson, *Phys. Rev.* **93**, 46 (1954).

<sup>6</sup> L. D. Ellerbeck, H. R. Shanks, P. H. Sidles, and G. C. Danielson, *J. Chem. Phys.* **35**, 298 (1961).

<sup>7</sup> M. Atoji and R. E. Rundle, *J. Chem. Phys.* **32**, 627 (1960).

<sup>8</sup> A. R. Mackintosh, *J. Chem. Phys.* **38**, 1991 (1963).

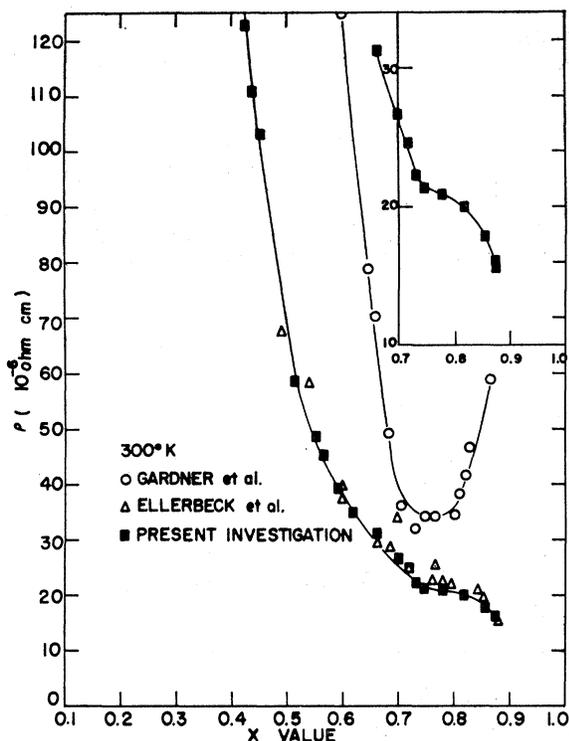


FIG. 1. Resistivity of  $\text{Na}_x\text{WO}_3$  as a function of sodium concentration at 300°K.

erties the results of ordering? Second, if homogeneous  $\text{Na}_x\text{WO}_3$  single crystals were used for Hall-coefficient measurements, would the results be the same as the results found by Gardner and Danielson?<sup>5</sup>

In answer to the preceding questions, this paper reports the electrical resistivities, the Hall coefficients, and the room-temperature Seebeck coefficients of very homogeneous single crystals of  $\text{Na}_x\text{WO}_3$ . Since Shanks *et al.*<sup>9</sup> have shown that the metallic behavior of the alkali tungsten bronzes should extend to  $x$  values as low as  $x=0.25$ , we have extended the measurements of the electrical properties of  $\text{Na}_x\text{WO}_3$  to include the tetragonal I structure ( $0.48 > x > 0.25$ ).

#### EXPERIMENTAL PROCEDURE

The  $\text{Na}_x\text{WO}_3$  single crystals were prepared by electrolytic reduction from a mixture of reagent-grade sodium tungstate and tungsten trioxide. Each  $\text{Na}_x\text{WO}_3$  single crystal was tested for sample homogeneity by the procedure suggested by Ellerbeck *et al.*<sup>6</sup> The percent deviation  $\Delta$ , defined as the ratio of the average deviation to the average resistivity, was less than 5% for each single crystal. However, for the samples which had an  $x$  value larger than  $x=0.65$  the percent deviation was less than 2% (with the exception of sample 230-C2,  $x=0.817$ , where  $\Delta=3.9\%$ ).

<sup>9</sup> H. R. Shanks, P. H. Sidles, and G. C. Danielson, *Advan. Chem. Ser.* **39**, 237 (1963).

The resistivity at 300 and 773°K was measured by a standard two-probe technique. The Hall coefficient and the resistivity at low temperatures were measured for each crystal by a Hall apparatus which used an ac electric current and a dc magnetic field. This ac Hall apparatus<sup>10</sup> was designed to measure ac voltages having magnitudes from  $10^{-3}$  to  $10^{-9}$  V by a null-balance technique.

The absolute Seebeck coefficients of  $\text{Na}_x\text{WO}_3$  were measured with respect to the Seebeck coefficient of copper. The details of the Seebeck-coefficient measurements as well as the results as a function of the temperature are to be reported in another paper.<sup>11</sup>

## RESULTS AND ANALYSIS

### Resistivity

The room-temperature resistivity of  $\text{Na}_x\text{WO}_3$  is plotted as a function of the sodium concentration in Fig. 1. Also shown in Fig. 1 is the room-temperature resistivity of  $\text{Na}_x\text{WO}_3$  measured by Gardner and Danielson<sup>5</sup> and the room-temperature resistivity of  $\text{Na}_x\text{WO}_3$  measured by Ellerbeck *et al.*<sup>6</sup> Ellerbeck *et al.* found that the difference (both in magnitude and in  $x$  dependence) between their resistivities and the resistivities measured by Gardner and Danielson was due to the inhomogeneity of the crystals used by Gardner and Danielson. The 18  $\text{Na}_x\text{WO}_3$  single crystals studied in the present investigation were electrically homogeneous, and the resistivities of these  $\text{Na}_x\text{WO}_3$  single crystals agreed with the resistivities which had been measured by Ellerbeck. There was, however, one notable difference. In the present research, each single crystal which had an  $x$  value larger than 0.65 had a deviation from the average resistivity which was less than or equal to 2%. The resistivity of these homogeneous single crystals is shown in Fig. 1 in the insert. At  $x=0.75$  there is a definite change in the slope of the resistivity-versus-sodium-concentration curve. A closer examination of Ellerbeck's data also reveals this same change in slope.

In Fig. 2, the conductivity of  $\text{Na}_x\text{WO}_3$  is plotted as a function of the sodium concentration for three different temperatures: 4.2, 300, and 733°K. Figure 2 also shows an enlarged section of the conductivity versus sodium concentration from  $x=0.7$  to  $x=0.9$ . For each of the three temperatures, the conductivity shows an anomaly at  $x=0.75$ . It is assumed that this anomaly in the conductivity at  $x=0.75$  is a consequence of the partial ordering of the sodium atoms.

At 4.2°K the thermal contribution to the resistivity is negligible so that the measured resistivity is equal to the residual resistivity. We assume that the contributions to the residual resistivity from impurities and lattice imperfections are small. This assumption seems to

<sup>10</sup> L. D. Muhlestein and P. H. Sidles (to be published).

<sup>11</sup> L. D. Muhlestein and G. C. Danielson (to be published).

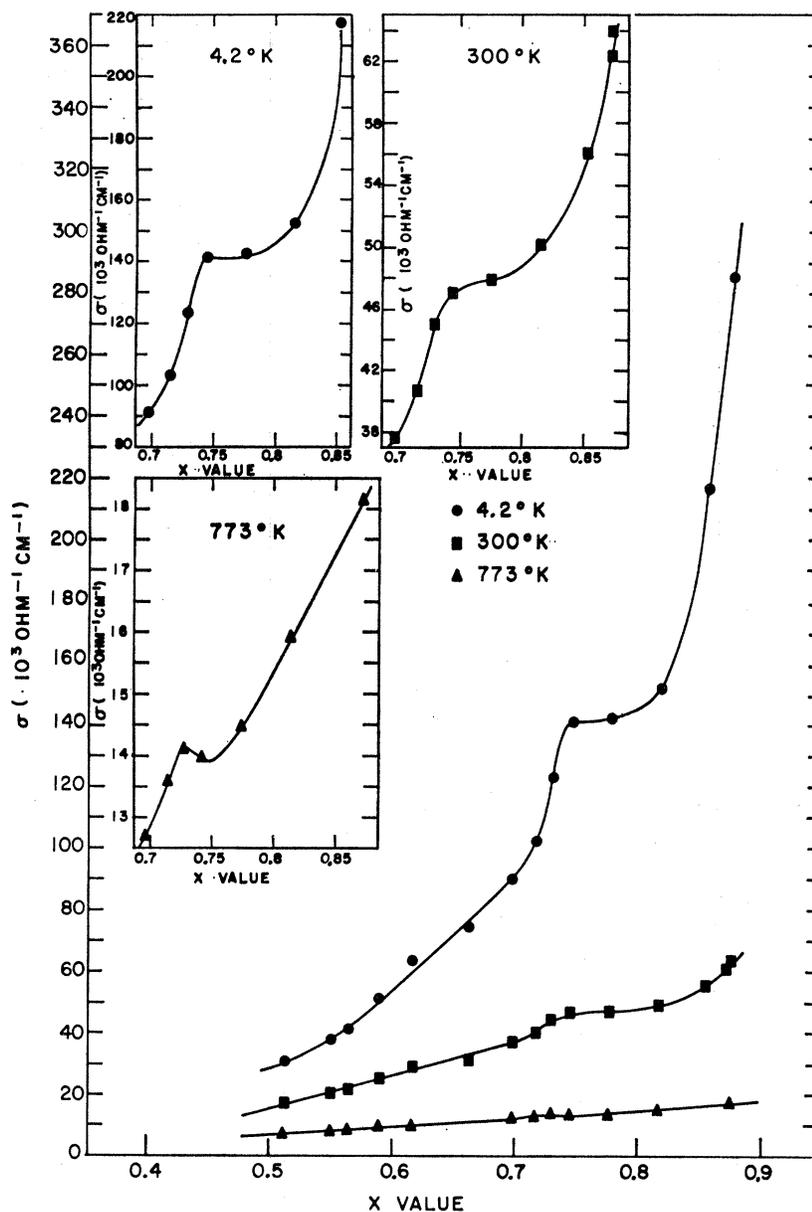


FIG. 2. Conductivity of  $\text{Na}_x\text{WO}_3$  as a function of sodium concentration at 4.2, 300, and 773°K.

be valid for  $\text{Na}_x\text{WO}_3$ , since the impurity contribution and the contribution from lattice imperfections would have no definite  $x$  dependence, whereas the resistivity at 4.2°K shows a strong  $x$  dependence. Thus, the major contribution to the residual resistivity would be the contribution from the electron-sodium-vacancy scattering. It is apparent from Fig. 2 that the conductivity at 4.2°K increases rapidly with increasing sodium concentration. As pointed out by Ellerbeck, this effect suggests that the sodium vacancies do act as scattering centers. Further, the residual resistivity is large, varying from 6% of the total resistivity at  $x=0.874$  to 24% of the total resistivity at  $x=0.513$ .

The thermal contribution as a function of the sodium concentration can be determined from the equation

$$\rho = \rho_{\text{Res}} + \rho_{\text{Th}}, \quad (1)$$

and is plotted in Fig. 3 as a function of the sodium concentration. There is a maximum in the thermal resistivity at  $x=0.75$ . This anomaly in the thermal resistivity would suggest that the partial ordering of the sodium atoms also affects the lattice vibrations.

The tetragonal I structure of  $\text{Na}_x\text{WO}_3$  is anisotropic. Thus, the resistivity can be resolved into two independent components,  $\rho_l$  and  $\rho_{l1}$ , where  $\rho_l$  is the resistivity perpendicular to the  $c$  axis (in the basal plane)

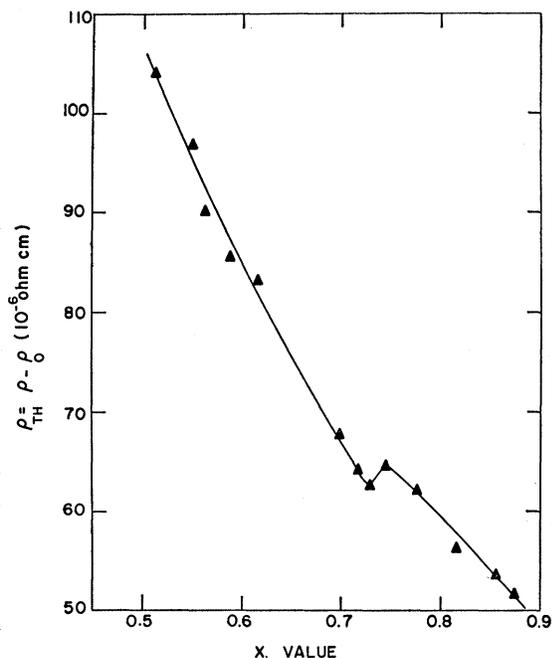


FIG. 3. Thermal contribution to the resistivity of  $\text{Na}_x\text{WO}_3$  as a function of sodium concentration.

and  $\rho_{11}$  is the resistivity parallel to the  $c$  axis. The anisotropy in the tetragonal I structure is evident in Fig. 4, where the resistivity is plotted as a function of

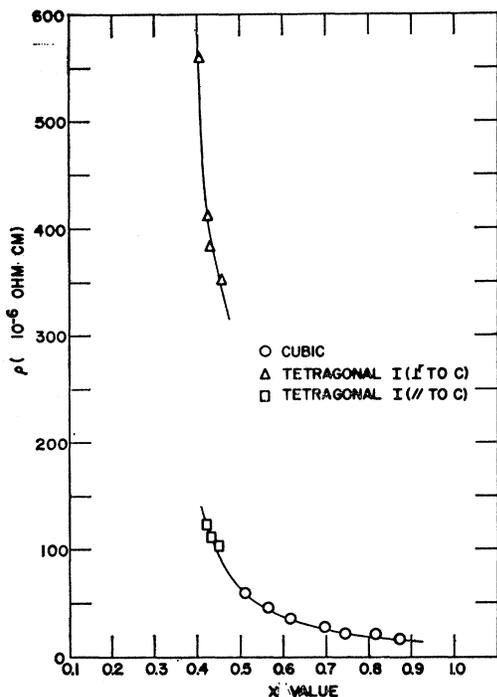


FIG. 4. Resistivity of  $\text{Na}_x\text{WO}_3$  as a function of sodium concentration at 300°K showing the anisotropy of the tetragonal I structure.

the sodium concentration at 300°K. The increase in the resistivity of the  $\text{Na}_x\text{WO}_3$  single crystals with an axis parallel to the  $c$  axis is similar to the increase in the resistivity of the cubic single crystals. However, the resistivity of the  $\text{Na}_x\text{WO}_3$  single crystals with an axis in the basal plane is much larger,  $\rho_{\perp} = 3.4 \rho_{\parallel}$ . This behavior is expected since, in the tetragonal I structure, the  $\text{WO}_3$  octahedra which share common corners have been rotated in the basal plane such that the tungsten-oxygen-tungsten angles are no longer 180°. Thus, the symmetry along the  $c$  axis remains about the same as the symmetry of the cubic structure while the symmetry in the basal plane has been changed considerably.

Figure 5 shows the resistivity of two tetragonal I  $\text{Na}_x\text{WO}_3$  single crystals as a function of the temperature. Sample 105-B2A,  $x = 0.423$ , has an axis parallel to the  $c$  axis while sample 109-A3,  $x = 0.405$ , has an axis in the basal plane. The temperature dependence of the resistivity for sample 105-B2A is very similar to the temperature dependence of the resistivity for the cubic  $\text{Na}_x\text{WO}_3$ . The resistivity for sample 109-A3 did, however, show a small but broad minimum at approximately 90°K. Both tetragonal I  $\text{Na}_x\text{WO}_3$  single crystals had a large residual resistivity.

#### Hall Coefficients

The room-temperature Hall coefficients of  $\text{Na}_x\text{WO}_3$  are plotted as a function of the sodium concentration in Fig. 6. Also shown in Fig. 6 are the Hall coefficients of  $\text{Na}_x\text{WO}_3$  measured by Gardner and Danielson<sup>5</sup> as well as the Hall coefficients of two of Gardner's samples measured during the present study. These Hall coefficients are as much as 20% lower than the Hall coefficients which were measured by Gardner and Danielson. Also, the  $x$  dependence of the Hall coefficients is different for the two investigations.

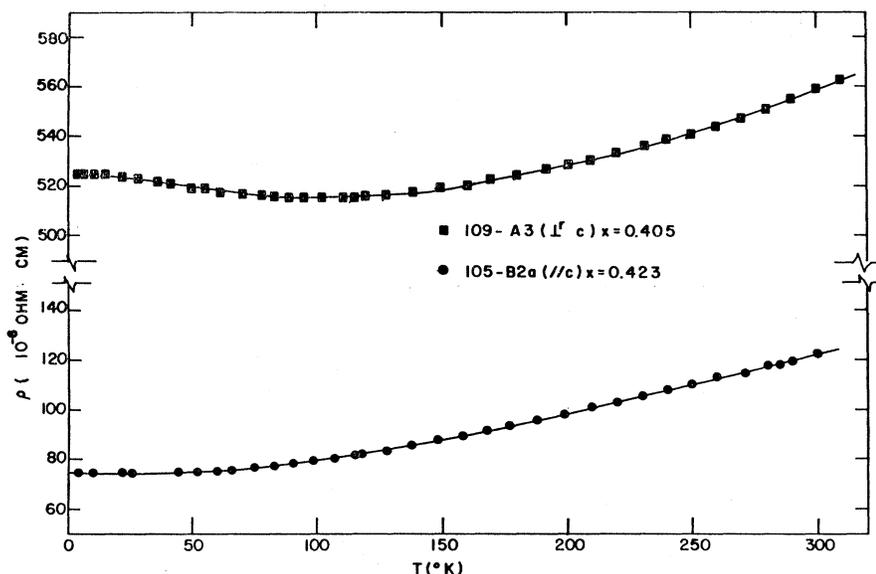
Gardner<sup>13</sup> noted that in his measurements only a slight shift in the position of the Hall probes gave appreciably different results for the Hall coefficient. Such effects would be expected in the case of inhomogeneous samples. Further, the Hall coefficients of two of Gardner's original samples were measured during the present study. The results are plotted in Fig. 6 and are within the experimental error of Gardner's data. We conclude, therefore, that the reason for the difference between the Hall coefficients reported in the present investigation and those reported earlier by Gardner and Danielson must be the inhomogeneity of the samples used in the earlier investigation. Accordingly, the Hall coefficients, like the resistivity, are affected by the homogeneity of the  $\text{Na}_x\text{WO}_3$  single crystals.

The Hall coefficients of three  $\text{Na}_x\text{WO}_3$  single crystals were measured as a function of the temperature from

<sup>12</sup> A. S. Ribnick, B. Post, and E. Banks, *Advan Chem. Ser.* 39, 246 (1963).

<sup>13</sup> W. R. Gardner, Ph.D. thesis, Iowa State University, 1953 (unpublished).

FIG. 5. Resistivity of two tetragonal I  $\text{Na}_x\text{WO}_3$  single crystals as functions of temperature from 4.2 to 300°K.



4.2 to 300°K. The results are shown in Fig. 7. Our results confirm the conclusion by Gardner and Danielson that the Hall coefficients of  $\text{Na}_x\text{WO}_3$  are independent of temperature from 4.2 to 300°K.

The number of sodium atoms per unit volume is given by  $N_a = x/a^3$ , where  $x$  is the sodium concentration and  $a$  is the lattice constant. Gardner and Danielson assumed the free-electron value for the Hall coefficient and thus determined an effective number of electrons given by  $n = 1/Re$ . They then plotted the number of electrons as determined from the Hall coefficient as a function of the number of sodium atoms per unit volume. Their results are plotted in Fig. 8. From the 1:1 correspondence, Gardner and Danielson concluded that each sodium atom contributed one electron to a conduction band. Hence, the number of conduction electrons would also be given by  $n = x/a^3$ .

Figure 8 also shows the reciprocal product  $1/Re$  plotted as a function of  $x/a^2$  for the Hall coefficients of the homogeneous  $\text{Na}_x\text{WO}_3$  single crystals that were measured during the present study. It is not evident from the Hall coefficients of homogeneous  $\text{Na}_x\text{WO}_3$  single crystals that there is a 1:1 correspondence between the number of conduction electrons and the number of sodium atoms. However, the Hall coefficient is given by

$$R = 1/ne, \quad (2)$$

only for the free-electron approximation, where the constant-energy surfaces are proportional to  $k^2$ . The observed  $x$  dependence of the reciprocal product  $1/Re$  would suggest that the Hall coefficients for  $\text{Na}_x\text{WO}_3$  are not given simply by Eq. (2).

The Hall mobility can be defined by the equation

$$\mu_H = R/\rho, \quad (3)$$

where  $R$  is the Hall coefficient and  $\rho$  is the resistivity. In Fig. 9 the Hall mobility as defined by Eq. (3) is plotted as a function of the sodium concentration at 300°K. The anisotropy of the tetragonal I structure is also evident in the Hall mobility with  $\mu_{11}/\mu_{\perp} = 2.86$ . Also, at  $x = 0.75$  there is an anomaly in the Hall mobility which is similar to the anomaly seen in the conductivity.

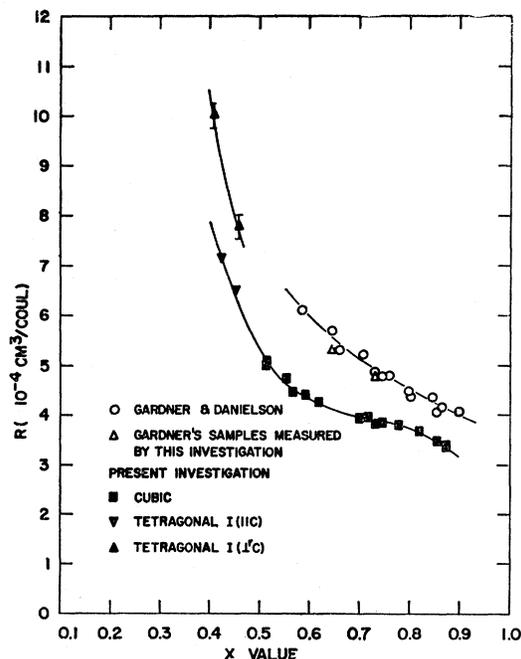


FIG. 6. Hall coefficients of  $\text{Na}_x\text{WO}_3$  as a function of sodium concentration.

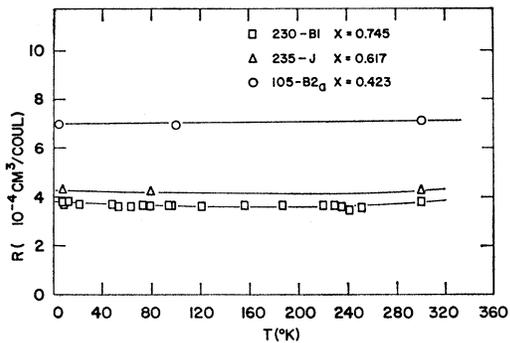


FIG. 7. Hall coefficients of three  $\text{Na}_x\text{WO}_3$  single crystals as functions of temperature from 4.2 to 300°K.

### Seebeck Coefficients

The room-temperature Seebeck coefficients of  $\text{Na}_x\text{WO}_3$  are plotted as a function of the sodium concentration in Fig. 10. At  $x=0.75$  there is a change in the slope of the curve showing Seebeck coefficients versus sodium concentration. Since the Seebeck coefficient is related to the conductivity by the expression

$$S = -\frac{\pi^2 k^2 T}{3e} \left[ \frac{\partial \ln \sigma(\epsilon)}{\partial \epsilon} \right]_{\epsilon=\epsilon_F}, \quad (4)$$

any anomalous behavior in the conductivity should be apparent in the Seebeck coefficient. Hence, the anomaly in the Seebeck coefficients at  $x=0.75$  must also be a consequence of the partial ordering of the sodium atoms.

### DISCUSSION

The neutron-diffraction studies of Atoji and Rundle<sup>7</sup> indicated that there is a partial ordering of the sodium atoms at  $x=0.75$  and that a superlattice is formed. The lattice constant of the superlattice is twice the original lattice constant. If the unit cell of the superlattice is chosen such that a sodium site is situated at each of the corners, then there are no sodium atoms at the  $(0,0,0)$  and the  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  sodium sites.

Since the lattice constant of the superlattice is twice the original lattice constant, the periodicity of the lattice potential in which the electrons move will be twice the ordinary lattice spacing. Consequently, the Brillouin zones will be split in half, and there will be new planes (superzones) where the energy is discontinuous.

The formation of superzones in connection with the ordering of  $\text{Na}_x\text{WO}_3$  was first suggested by Mackintosh.<sup>8</sup> Mackintosh pointed out that the sudden increase in the density of states at the Fermi energy at  $x=0.75$ <sup>14</sup> could be due to the onset of ordering and the consequent appearance of superzones. Mackintosh further suggested that the continual increase in the density of

states for  $x$  larger than 0.75 could be due to the fact that the electrons begin to occupy a second conduction band. In fact, after the ordering at  $x=0.75$ , a second conduction band would be expected since the appearance of the superzones would have the same effect as if the electrons had almost filled a first zone and had begun to spill over into a second zone. Thus, there would be two conduction bands: one which is nearly filled, where conduction is by holes, and one which is nearly empty, where conduction is by electrons.

Thus, the behavior of the conductivity of  $\text{Na}_x\text{WO}_3$  can be explained qualitatively in the following manner. For  $x$  less than 0.75, there is only one conduction band and the conductivity can be written as

$$\sigma = \frac{e^2}{12\pi^3 \hbar} \int_{FS} \Lambda dS. \quad (5)$$

Thus, the conductivity varies approximately as  $\Sigma \Lambda_f$ , where  $\Sigma$  is the area of the Fermi surface and  $\Lambda_f$  is an average mean free path at the Fermi surface.

We assume that each sodium atom contributes one electron to the conduction band. Therefore, it is reasonable to suppose that the area of the Fermi surface increases with increasing sodium concentration. Since  $\Sigma$  and  $\Lambda_f$  both increase with increasing sodium concentration, the conductivity would also increase with increasing sodium concentration.

At  $x=0.75$ , however, the sodium atoms are ordered and superzones are formed in the Brillouin zone. The effect of the energy gap across the superzone boundary is to decrease the conductivity. Thus, there may be a maximum in the conductivity near  $x=0.75$ . However,

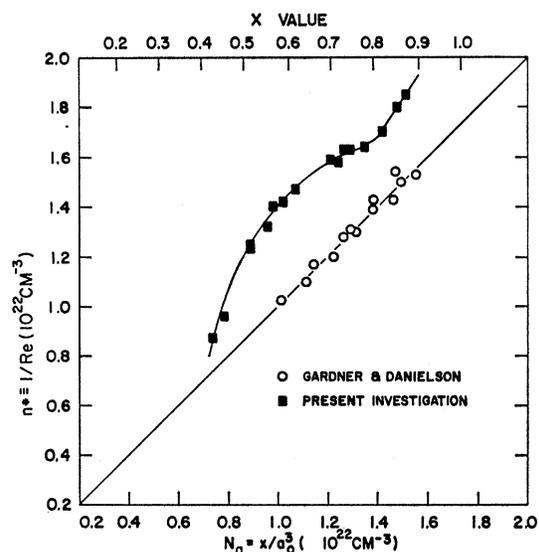


FIG. 8. Effective number of conduction electrons defined by  $n^* = 1/Re$  as a function of the number of sodium atoms per unit volume.

<sup>14</sup> R. W. Vest, M. Griffl, and J. F. Smith, J. Chem. Phys. 28, 293 (1958).

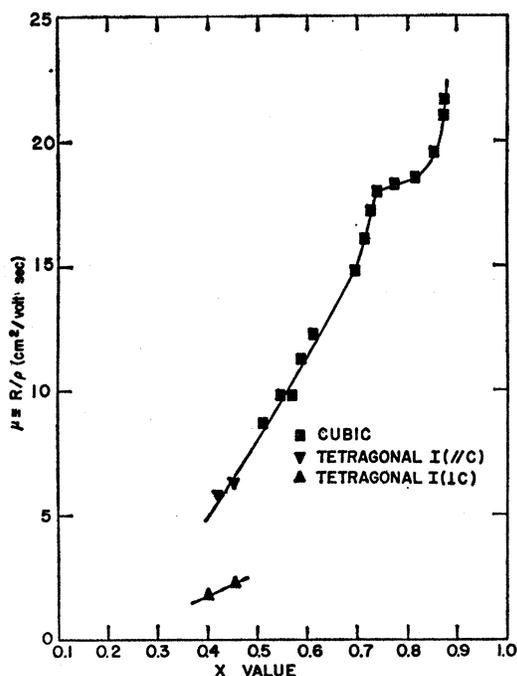


FIG. 9. Hall mobility of  $\text{Na}_x\text{WO}_3$  defined by  $\mu = R/\rho$  as a function of sodium concentration.

if the energy gap is small, the conductivity may just level off.

For  $x$  larger than 0.75, there are two conduction bands which contribute to the conductivity. The electrons in the nearly filled band will have a larger effective mass than the electrons in the nearly empty band. Thus, the contribution to the conductivity from the nearly filled band will be less than the contribution from the nearly empty band. The total conductivity will, therefore, increase again with increasing sodium concentration.

Hence, one would expect that the conductivity of  $\text{Na}_x\text{WO}_3$  would increase with increasing sodium concentration for  $x$  less than 0.75. In the vicinity of  $x=0.75$  there may be a maximum in the conductivity or, depending on the magnitude of the energy gap across the superzones, the conductivity may just level off. For  $x$  larger than 0.75, the conductivity would increase again with increasing sodium concentration. Figure 2 shows that these conclusions are in accord with the experimental results. These conclusions are also in agreement with a model proposed for  $\text{Na}_x\text{WO}_3$  by Goodenough.<sup>15</sup>

The Hall coefficient for a crystal with cubic symmetry and a nonspherical Fermi surface in low magnetic fields can be written as<sup>16</sup>

$$R = \sigma_H / \sigma_0^2, \quad (6)$$

<sup>15</sup> J. B. Goodenough, Bull. Soc. Chim. France 4, 1200 (1965).

<sup>16</sup> J. M. Ziman, Advan. Phys. 10, 1 (1961).

where

$$\sigma_0 = \frac{e^2}{12\pi^3\hbar} \int_{FS} V_k \tau_k dS \quad (7)$$

and

$$\sigma_H = \frac{e^3}{4\pi^3} \int_{FS} \tau^2 \{ V_x^2 M_{yy}^{-1} - V_x V_y M_{yx}^{-1} \} \frac{dS}{V_k}. \quad (8)$$

In the above equations, the magnetic field is taken to be in the  $z$  direction, the current is taken to flow in the  $x$  direction, and the Hall voltage is measured in the  $y$  direction.

The inverse mass tensor is defined by

$$M_{yy}^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_y^2} \quad (9)$$

and

$$M_{yx}^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_y \partial k_x}. \quad (10)$$

Thus, the Hall coefficient varies approximately as  $eR \sim -M^{-1}/\Sigma v_f$ , where  $\Sigma$  is the area of the Fermi surface,  $v_f$  is an average velocity at the Fermi surface, and  $M^{-1}$  is the inverse mass tensor averaged over the entire Fermi surface.

For a distorted Fermi surface there may be sections of the surface which have positive curvature (positive inverse mass tensor) and sections of the surface which have negative curvature (negative inverse mass tensor). The average inverse mass tensor will contain contributions from both sections of the surface and will be smaller than the inverse of the corresponding free-electron mass. Also, the area of a distorted Fermi surface will be larger than the area of the corresponding free-electron sphere since the volume must remain the same. Thus, for a distorted Fermi surface the magnitude of the Hall coefficient would be smaller than the corresponding free-electron value, and the reciprocal product  $1/Re$  would give an effective number of conduction

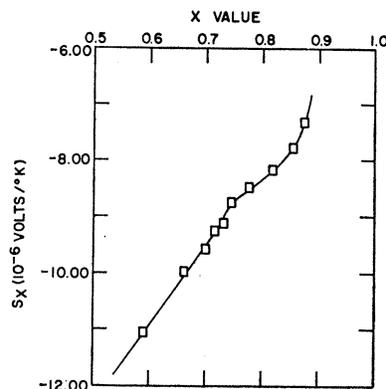


FIG. 10. Room-temperature Seebeck coefficients of  $\text{Na}_x\text{WO}_3$  as a function of sodium concentration.

electrons which would be larger than the actual number of conduction electrons.

For  $\text{Na}_x\text{WO}_3$  it appears that the constant energy surfaces are not simply proportional to  $k^2$ . Thus, one would expect that the effective number of conduction electrons determined from the Hall coefficients would be larger than the actual number of conduction electrons. Figure 8 shows this conclusion to be in accord with the experimental results.

We assume that the area of the Fermi surface increases with increasing sodium concentration. Since the Fermi surface becomes more and more distorted as it expands toward the zone boundary, the sections of the Fermi surface with a negative curvature will increase and will contribute larger negative contributions to the average inverse mass tensor. Thus, the magnitude of the average inverse mass tensor will decrease with increasing sodium concentration and the area of the Fermi surface will increase with increasing sodium concentration. Hence, the magnitude of the Hall coefficients will decrease with increasing sodium concentration or the effective number of conduction electrons will increase with increasing sodium concentration as shown in Fig. 8.

At  $x=0.75$  the sodium atoms are ordered and another conduction band is formed. The band which is nearly empty, where conduction is by electrons, will contribute a negative contribution to the Hall coefficient. The band which is nearly filled, where conduction is by holes, will contribute a positive contribution to the Hall coefficient. The negative contribution to the Hall coefficient is dominant, but the magnitude of the Hall coefficient decreases faster for  $x$  larger than 0.72. This more rapid decrease in the Hall coefficient is seen in

the increase in the effective number of conduction electrons for  $x$  larger than 0.75 (see Fig. 8).

### SUMMARY

We have shown, in answer to the first question suggested at the beginning of this paper, that if homogeneous  $\text{Na}_x\text{WO}_3$  single crystals are used for measurements, then one can observe anomalies in the electrical transport properties which are a result of the ordering of the sodium atoms. If the sodium atoms were completely ordered at  $x=0.75$ , then one would expect large anomalies in the transport properties. The anomalies which we have observed are, however, quite small. Thus, the experimental data confirms the fact that there is only a partial ordering of the sodium atoms.

Secondly, we have shown that the homogeneity of the  $\text{Na}_x\text{WO}_3$  single crystals affects the Hall coefficients. The Hall coefficients for homogeneous  $\text{Na}_x\text{WO}_3$  single crystals do not suggest a 1:1 correspondence between the number of conduction electrons and the number of sodium atoms. However, it is reasonable to assume that each sodium atom is completely ionized. We thus assume that the number of "free" electrons is equal to the number of sodium atoms but conclude that the electronic properties of  $\text{Na}_x\text{WO}_3$  cannot be explained satisfactorily by a simple free-electron approximation.

### ACKNOWLEDGMENTS

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