PHYSICAL REVIEW VOLUME 160, NUMBER 3 15 AUGUST 1967

Seebeck Effect in Sodium Tungsten Bronze*

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(Received 16 February 1967)

The Seebeck coefficients of metallic Na_xWO_3 were measured as functions of the sodium concentration x from $x=0.9$ to $x=0.4$, and as functions of the temperature from 4.2 to 300°K. The diffusion contribution did not confirm the $x^{-2/3}$ dependence predicted by free-electron theory and suggested by earlier data. The lattice contribution at low temperatures contained a term due to normal electron-phonon processes and a term due to umklapp electron-phonon processes. The umklapp phonon drag increased with increasing sodium concentration, a result that would be expected if the Fermi surface increases with increasing sodium concentration. The Seebeck coefficient of tetragonal crystals was anisotropic with $S_\perp/S_\parallel=1.3$ at 300°K.

INTRODUCTION

THE transport properties of cubic sodium tungsten bronze, Na_xWO_3 $(1.0>x>0.48)$, have been studied extensively.[1–6] In particular, the Seebeck coefficients of cubic Na_xWO_3 were measured by Shanks *et al.*[3] at 300°K. They found that the Seebeck coefficients seemed to vary as $x^{-2/3}$, as predicted by the free-electron model. Shanks *et al.*[3] concluded that for the electronic properties of Na_xWO_3 the free-electron model seemed to be applicable even though it did not account for the density of states at the Fermi energy[5] nor the magnetic susceptibility of the conduction electrons.[6] Recent measurements of the Hall coefficients of Na_xWO_3 by Muhlestein and Danielson[4] indicated that the free electron model is also unsatisfactory for the Hall coefficients. Thus, it seemed desirable to reexamine the x dependence of the room temperature Seebeck coefficients of Na_xWO_3, as well as to measure the temperature dependence of the Seebeck coefficients for various sodium concentrations. In this paper we report the Seebeck coefficients of metallic Na_xWO_3 as functions of sodium concentration and temperature for single crystals carefully selected to be homogeneous in electrical resistivity. The temperature range was from 15° to 340°K. The sodium concentration ranged from $x=0.9$ to $x=0.4$ and included both the cubic and the tetragonal I structures.

EXPERIMENTAL PROCEDURE

The Na_xWO_3 single crystals were prepared by electrolytic reduction from a mixture of reagent grade sodium tungstate and tungsten trioxide. Each Na_xWO_3 single crystal was tested for sample homogeneity by the procedure suggested by Ellerbeck *et al.*[2] The ratio of the average deviation to the average resistivity was less than 5% for each sample.

The Seebeck coefficient is defined by the equation

$$\mathbf{E}=-S\nabla T, \tag{1}$$

where $\mathbf{E}$ is the electric field which is produced across a conductor by the presence of a temperature gradient. If we integrate Eq. (1) around the closed circuit which consists of two copper potential leads and the sample and if the temperature gradient is small, then we obtain

$$\Delta V_{x\,\mathrm{Cu}}=-(S_x-S_{\mathrm{Cu}})\Delta T. \tag{2}$$

In Eq. (2), S_x is the absolute Seebeck coefficient of the sample, S_{Cu} is the absolute Seebeck coefficient of the copper potential leads, $\Delta V_{x\,\mathrm{Cu}}$ is the potential measured across the sample, and ΔT is the temperature difference across the sample. Thus, the absolute Seebeck coefficients of Na_xWO_3 were determined from the relation

$$S_x=S_{\mathrm{Cu}}-\Delta V_{x\,\mathrm{Cu}}/\Delta T. \tag{3}$$

The Seebeck coefficients of the copper potential leads were calibrated from 4.2 to 300°K against the Seebeck coefficients of lead determined by Christian *et al.*[7] The temperature difference was measured by two coppergold (0.07 at % iron) or two copper-constantan thermocouples which were placed directly at each end of the sample. At low temperatures the magnitude of $\Delta V_{x\,\mathrm{Cu}}$ was of the order of 1 microvolt and could be measured to 0.01 μV. The thermocouple potential difference corresponding to ΔT was of the order of 10 μV and could be measured to 0.1 μV.

RESULTS AND ANALYSIS

The Seebeck coefficients of Na_xWO_3 are plotted as functions of the temperature from 15 to 300°K in Fig. 1. The seven samples with x between 0.875 and 0.512 were cubic Na_xWO_3. The three samples with x between

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* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2049.

† Atomic Energy Commission Postdoctoral Fellow.

[1] W. R. Gardner and G. C. Danielson, Phys. Rev. **93**, 46 (1954).

[2] L. D. Ellerbeck, H. R. Shanks. P. H. Sidles, and G. C. Danielson, J. Chem. Phys. **35**, 298 (1961).

[3] H. R. Shanks, P. H. Sidles, and G. C. Danielson, Advan. Chem. Ser. **39**, 237 (1963).

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[5] R. W. Vest, M. Griffel, and J. F. Smith, J. Chem. Phys. **28**, 293 (1958).

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[7] J. W. Christian, J. P. Jan, W. B. Pearson, and I. M. Templeton, Proc. Roy. Soc. (London) **A245**, 213 (1958).

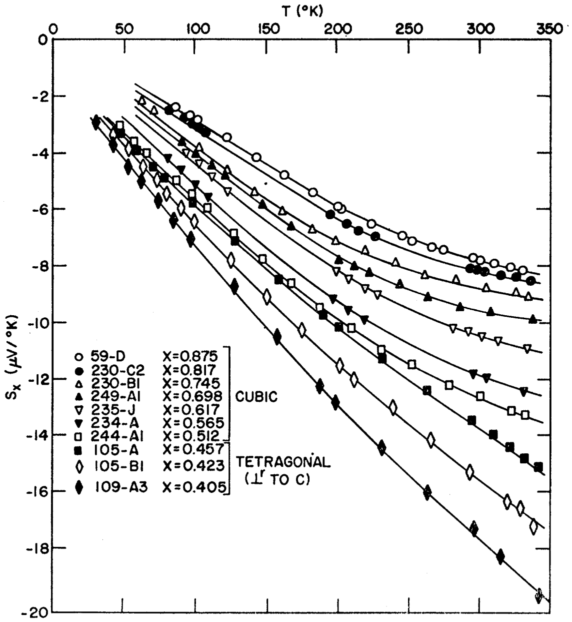

FIG. 1. Seebeck coefficients of Na_xWO_3 as functions of temperature from 50° to 340°K.

0.457 and 0.405 were tetragonal I Na_xWO_3 with the axis of the sample in the basal plane.

In Fig. 2 the Seebeck coefficients of the Na_xWO_3 single crystals are plotted as functions of the temperature from 15 to 60°K on an expanded scale. Besides the usual diffusion contribution to the Seebeck coefficients, which is proportional to the temperature, there is another contribution which is believed to be a lattice or a phonon-drag contribution. In order to separate the diffusion contribution and the lattice contribution, the total Seebeck coefficient is assumed to be the sum of the diffusion contribution and the lattice contribution.[8] The diffusion contribution S_d is proportional to the temperature. Hanna and Sondheimer[9] have shown that the lattice contribution from normal electron-phonon processes increases from low temperatures as T^3 and decreases at higher temperatures as T^{-1}. Similarly, Bailyn[10] has shown that the lattice contribution from umklapp electron-phonon processes decreases at higher temperatures as T^{-1}. Thus, we assume that the total lattice contribution S_g decreases as T^{-1} for temperatures larger than $\Theta_D/10$. The total Seebeck coefficient, for temperatures larger than $\Theta_D/10$, can then be written as

$$S=AT+BT^{-1}, \tag{4}$$

where $S_d=AT$ and $S_g=BT^{-1}$. We can write Eq. (4) in the form

$$ST=B+AT^2. \tag{5}$$

The slope A of the curve ST versus T^2 will give the diffusion contribution to the Seebeck coefficient, and the lattice contribution can then be determined from

$$S_g=S-AT, \tag{6}$$

where S is the total measured Seebeck coefficient.

In Fig. 3 the product ST is plotted as a function of T^2 for sample 59-$D(x=0.875)$. The resulting straight line had a slope equal to -2.93×10^{-2} μV/°K². Thus, the diffusion contribution for sample 59-D was

$$S_d=-2.93\times10^{-2}T\ \mu\text{V}/°\text{K}, \tag{7}$$

where T is the temperature in degrees Kelvin. The lattice contribution for sample 59-D was then given by

$$S_g=S+2.93\times10^{-2}T. \tag{8}$$

In Fig. 4 the total Seebeck coefficient, the calculated diffusion contribution, and the resulting lattice contribution are plotted as functions of the temperature from 15 to 60°K for sample 59-D.

The lattice contribution for each Na_xWO_3 single crystal was determined in this way. Figure 5 shows the lattice contributions as functions of the temperature from 15 to 60°K. The lattice contribution for high

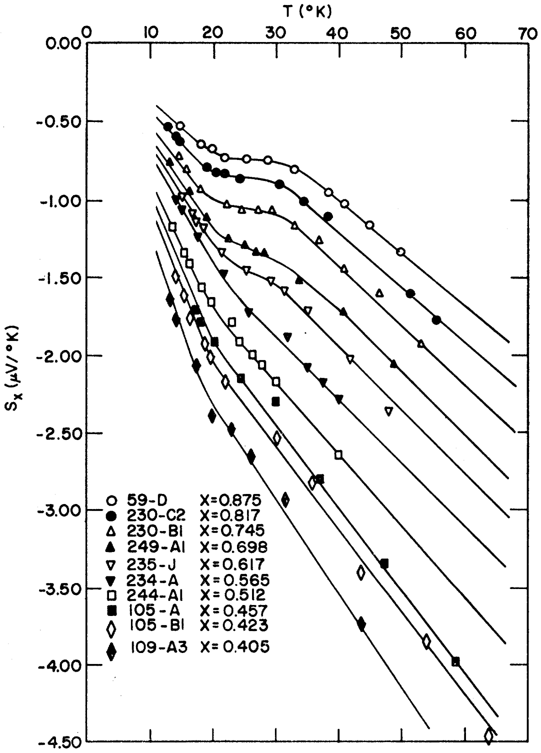

FIG. 2. Seebeck coefficients of Na_xWO_3 as functions of the temperature from 15 to 60°K. Besides the usual diffusion contribution to the Seebeck coefficients, which is proportional to the temperature, there is also a phonon-drag contribution.

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[8] D. K. C. MacDonald, *Thermoelectricity: An Introduction to the Principles* (John Wiley & Sons, Inc., New York, 1962), pp. 113, 114.

[9] I. I. Hanna and E. H. Sondheimer, Proc. Roy. Soc. (London) **A239**, 247 (1957).

[10] M. Bailyn, Phys. Rev. **112**, 1587 (1958).

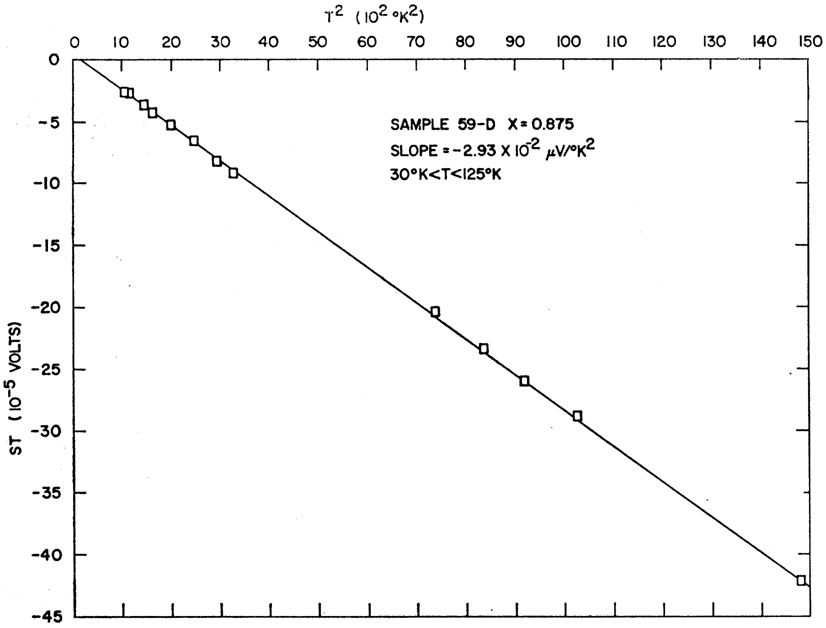

FIG. 3. The product of the Seebeck coefficient and the temperature as a function of the square of the temperature for sample 59-D. The slope of the curve will give the diffusion contribution to the Seebeck coefficient.

sodium concentrations is seen to consist of both a negative term and a positive term. Bailyn[10] showed that all normal electron-phonon processes gave a negative term to the lattice Seebeck coefficient while all umklapp electron-phonon processes gave a positive term to the lattice Seebeck coefficient. Thus, the negative term in the lattice Seebeck coefficient of Na_xWO_3 is assumed to be due to normal electron-phonon processes (*N* processes) while the positive term is assumed to be due to umklapp electron-phonon processes (*U* processes). As the sodium concentration is decreased, the umklapp phonon-drag decreases while the normal phonon-drag increases.

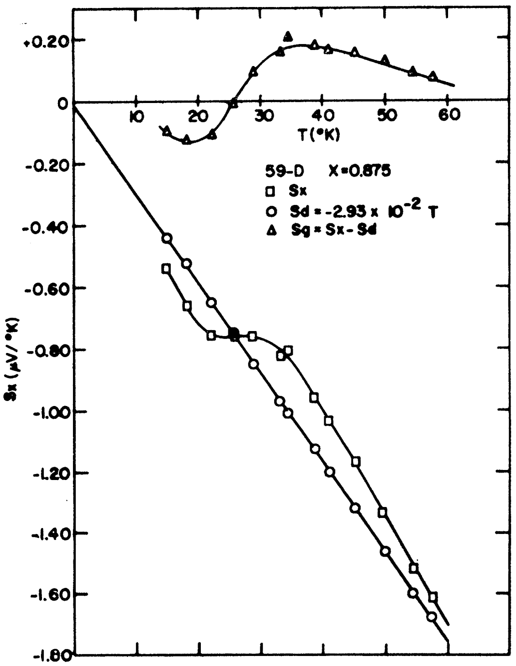

FIG. 4. Total Seebeck coefficients (S_x), diffusion contribution (S_d), and lattice contribution (S_g) as functions of the temperature for sample 59-D ($x=0.875$).

In Fig. 6 the coefficients A, from which the diffusion contributions were determined, and the phonon-drag contributions at 19°K are plotted as functions of the sodium concentration. Both contributions increase with decreasing sodium concentration. The diffusion contribution to the Seebeck coefficient does not depend explicitly on the details of the lattice. Hence, the diffusion contribution varies smoothly as the structure changes from cubic to tetragonal I at $x=0.48$. However, the phonon-drag contribution is related to the details of the lattice and the structure change from cubic to tetragonal I is seen in the sharp increase in the normal phonon-drag contribution starting at $x=0.48$.

The tetragonal I structure of Na_xWO_3 is anisotropic, and the Seebeck coefficient can be resolved into two independent components. At 300°K the ratio of the two independent components was found to be $S_\perp/S_\parallel=1.3$ where $S_\perp$ is the Seebeck coefficient of the sample when the temperature gradient is in the basal plane and $S_\parallel$ is the Seebeck coefficient of the sample when the temperature gradient is parallel to the *c* axis.

DISCUSSION

The total Seebeck coefficients of the Na_xWO_3 single crystals are plotted in Fig. 7 as functions of the sodium concentration for six different temperatures. At room temperature the magnitudes of the Seebecks coefficients

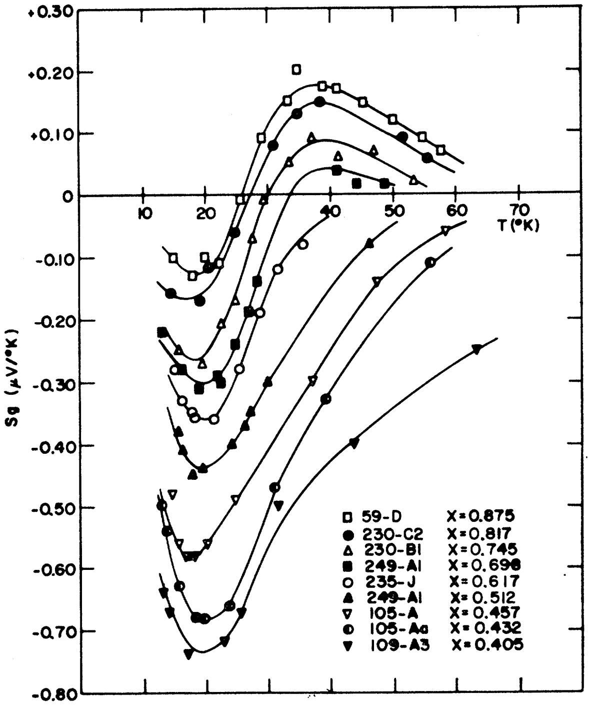

FIG. 5. Lattice contributions to the total Seebeck coefficients of Na_xWO_3 as functions of the temperature from 15 to 60°K. Note that the lattice contributions consist of both a negative term and a positive term.

start to increase rapidly with decreasing sodium concentration. Shanks *et al.*[3] had found that the Seebeck coefficients at 300°K seemed to vary as $x^{-2/3}$ as predicted by the free-electron model. However, because of the limited range of x values and the scatter in the data, the function x^{-n}, where n is a fraction, is quite insensitive to the exponent. Thus, it is difficult to determine the x dependence of the Seebeck coefficients from the experimental data. However, the results of the present investigation indicated that the Seebeck coefficients at 300°K vary faster than $x^{-2/3}$.

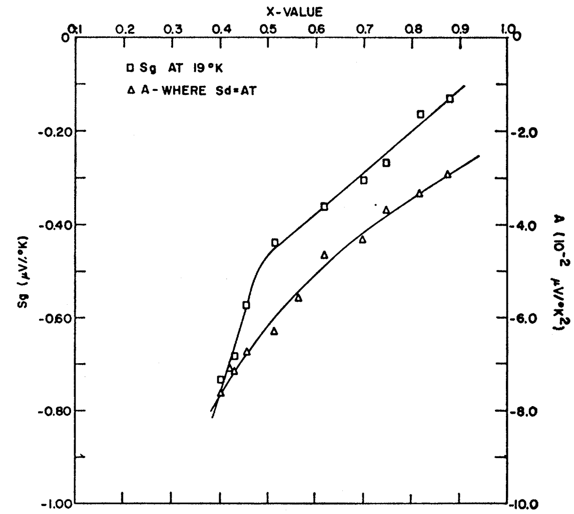

FIG. 6. Coefficients A and lattice contributions (S_g) at 19°K as functions of the sodium concentration. The lattice contribution S_g changes slope when the crystal structure changes from cubic to tetragonal I at $x=0.48$.

The measured Seebeck coefficients can, however, be compared to the free-electron values of the Seebeck coefficient in the following way. For the free-electron approximation, the diffusion contribution to the Seebeck coefficient is

$$S_d=\frac{\pi^2}{3}\frac{k^2}{e}\frac{T}{\epsilon_F}. \tag{9}$$

If the Fermi energy for free electrons is submitted into Eq. (9), the diffusion contribution becomes

$$S_d=\frac{2}{3}\left(\frac{\pi}{3}\right)^{2/3}\frac{m^*k^2T}{eh^2}n^{-2/3}. \tag{10}$$

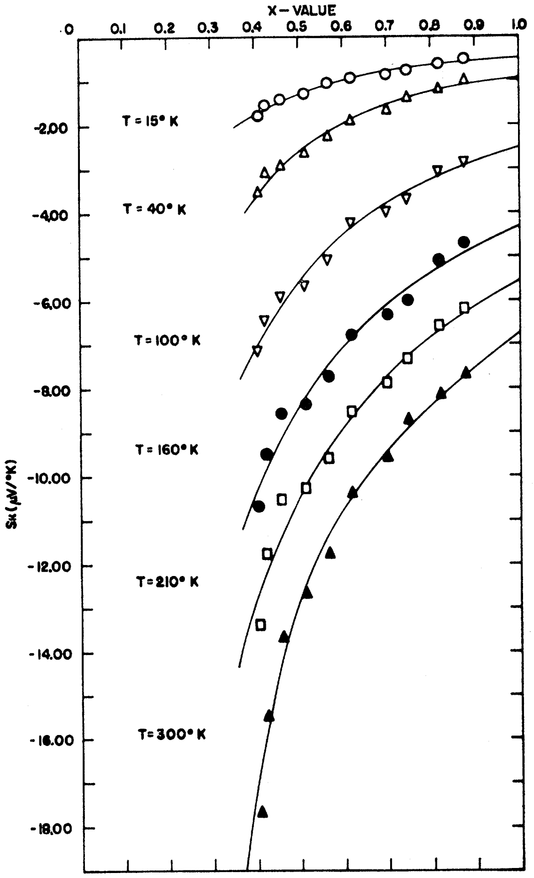

FIG. 7. Total Seebeck coefficients of Na_xWO_3 as functions of the sodium concentration for 15, 40, 100, 160, 210, and 300°K.

We assume that each sodium atom contributes one electron to the conduction band. Thus, the number of conduction electrons per unit volume is $n=x/a^3$, where

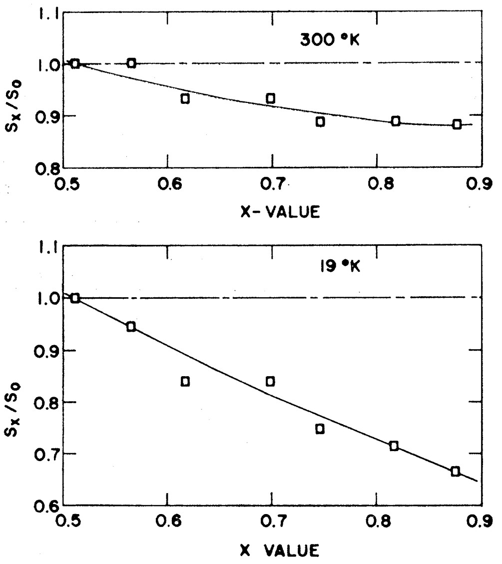

FIG. 8. The ratio of the observed diffusion contribution to the Seebeck coefficient to the free-electron value of the Seebeck coefficient as functions of the sodium concentration (the dashed lines represent $S_x/S_0=1$).

x is the sodium concentration and a is the lattice constant. The effective mass can be written as $m^*=bm$ where m is the mass of a free electron and b is an adjustable parameter. If the numerical values of the physical constants are substituted into Eq. (10), then the free electron value for the diffusion Seebeck coefficient is

$$S_0=10.02\times 10^{-9}\, bTx^{-2/3}\ \mathrm{V/°K}. \qquad (11)$$

At 300°K the lattice contribution to the Seebeck coefficient should be negligible, and the measured Seebeck coefficient should be just the diffusion contribution. Also, for low temperatures (less than $\Theta_D/10$) the diffusion contribution can be separated from the lattice contribution. Hence, at both 300°K and at some low temperature (say 19°K) the measured diffusion contribution to the Seebeck coefficient can be compared with the free-electron value. The comparison may be described by the ratio S_x/S_0 which is plotted in Fig. 8 as a function of the sodium concentration. For both temperatures the adjustable parameter b was arbitrarily chosen such that $S_x/S_0=1$ when $x=0.512$. From Fig. 8 it is evident that there is no value of b which could be chosen so as to make $S_x/S_0=1$ for all values of x. Thus, the observed values of the diffusion contribution to the Seebeck coefficient do not correspond to the free-electron values for the diffusion contribution. Hence, we conclude that the Seebeck coefficients of Na_xWO_3 as a function of the sodium concentration cannot be explained satisfactorily by the free-electron approximation.

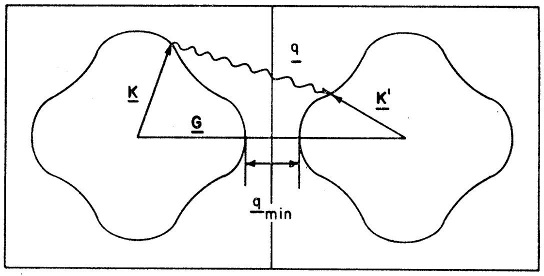

FIG. 9. A schematic representation showing the minimum value of q for which a U process can occur. As the electron concentration increases, $q_{\min}$ decreases and the umklapp processes become more probable.

Ziman[11,12] has pointed out that the lattice contribution to the Seebeck coefficient is very sensitive to any distortion of the Fermi surface and is one of the best indices of the shape of the Fermi surface. If only electron-phonon interactions are considered, then the lattice contribution to the Seebeck coefficient is given by Ziman[12] as

$$S_g=-\frac{k4\pi^4}{en_a{}^5}\left(\frac{T}{\Theta_D}\right)^3\frac{\langle K\cdot q\rangle}{\langle q^2\rangle}, \qquad (12)$$

where $\mathbf{K}=\mathbf{k}-\mathbf{k}'$ and the terms in the brackets refer to averages over all electron-phonon scattering processes. When considering both N processes and U processes, Bailyn[10] found that all N processes gave a negative term to the Seebeck coefficient while all U processes provided a positive term. Thus, the sign of the lattice Seebeck coefficient is a delicate balance between the contribution of N processes and U processes. This balance between the contribution of N processes and U processes depends on the form of the electron-phonon interactions and, thus, on the shape of the Fermi surface.

Consider a simple but nonspherical Fermi surface in the repeated zone scheme as shown in Fig. 9. The condition for N processes is that

$$\mathbf{k}'-\mathbf{k}=q,$$

while for U processes

$$\mathbf{k}'-\mathbf{k}-\mathbf{G}=q,$$

where $\mathbf{G}$ is a reciprocal lattice vector, $\mathbf{q}$ is the phonon wave vector, and $\mathbf{k}$ and $\mathbf{k}'$ are the initial and final wave vectors for the electrons. The minimum value of $\mathbf{q}$ for which a U process can occur is twice the distance in $\mathbf{k}$ space between the Fermi surface and the zone boundary. This distance is marked by $q_{\min}$ in Fig. 9. As the value of $q_{\min}$ decreases, the probability of U processes occurring will increase. Thus, the contribution of U processes to the lattice Seebeck coefficient will increase as $q_{\min}$ decreases.

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 of Na_xWO_3 increases with increasing sodium concen-

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[11] J. M. Ziman, *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), pp. 296–305.

[12] J. M. Ziman, Phil. Mag. 4, 371 (1959).

tration. As the sodium concentration increases, the minimum distance, $q_{\min}$, between the Fermi surface and the zone boundary decreases. The contribution of U processes to the lattice Seebeck coefficient will, therefore, increase with increasing sodium concentration. Thus, the lattice Seebeck coefficient should show an increase in the positive phonon-drag contribution with increasing sodium concentration. This behavior is seen in the lattice Seebeck coefficient of Na_xWO_3 (see Fig. 5). For low sodium concentrations there is only a negative contribution to the lattice Seebeck coefficient. However, as the sodium concentration increases, the positive phonon-drag contribution also increases.

We conclude that the Fermi surface of Na_xWO_3 is more complicated than the free-electron sphere, but that the x dependence of the lattice Seebeck coefficient can be qualitatively understood if we assume that the Fermi level increases with increasing number of free electrons.

ACKNOWLEDGMENTS

We wish to thank Dr. R. Fuchs and Dr. A. L. Trego for their helpful discussions. Thanks are also due to O. M. Sevde for his technical assistance, and Miss J. E. Brown for her help in preparing the Na_xWO_3 single crystals.

PHYSICAL REVIEW VOLUME 160, NUMBER 3 15 AUGUST 1967

Electron Energy Levels in Cu_3Au†*

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(Received 30 January 1967)

Electron energy levels in perfectly ordered Cu_3Au have been calculated using the modified-plane-wave (MPW) method for the majority of points in the Brillouin zone and using the orthogonalized-plane-wave (OPW) method for some of the lower symmetry points. The calculation has been done for the equivalent of 512 points in the reciprocal-space lattice. A muffin-tin model potential has been used. This was constructed from the atomic potentials of Herman and Skillman who did a self-consistent calculation based on the Slater version of the Hartree-Fock equations. This version includes an averaged exchange term. $E(\mathbf{k})$ curves are shown. The Fermi level has been computed to be -0.39 Ry. The resulting Fermi surface compares very well with the simplified surface constructed by Harrison by folding the copper Fermi surface in accord with the new lattice. Calculations were also carried out at a limited number of points for copper using both the Herman-Skillman and the Chodorow potentials in order to examine the sensitivity of the results to difference in potential. The two compare within about 0.04 Ry near the Fermi level but some d-like points differ by as much as 0.1 Ry.

CRYSTAL STRUCTURE AND POTENTIAL

In the present paper, the band structure of perfectly ordered Cu_3Au is calculated using the modified-plane-wave (MPW) method[1] in conjunction with the orthogonalized-plane-wave (OPW) method. The MPW method was used in order to guarantee convergence from above. However, the OPW method was found to be entirely satisfactory when used with accurate core states. The simple-cubic unit cell for Cu_3Au is shown in Fig. 1. There is one gold atom and three copper atoms associated with each lattice point. In this paper the origin is taken at a gold atom, $\boldsymbol{\tau}$ vectors describe the positions of unit cells, and $\mathbf{s}_\nu$ vectors describe the positions of the basis atoms within a unit cell. As the unit cell is simple cubic, the Brillouin zone is also simple cubic. This is shown in Fig. 2 with the points of high symmetry labeled in the Bouckaert, Smoluchowski, and Wigner (BSW) notation.[2]

The one-electron approach is used. The crystal potential is constructed from the atomic potentials of Herman and Skillman[3] (HS) using the muffin-tin model. In this model we surround the individual atoms with nonoverlapping spheres whose radii are chosen so that the potentials match at the point of contact. Inside each of these spheres we take the crystal potential to be the potential of that particular atom as a free ion and outside the spheres we take the potential to be a constant. The HS potentials were modified slightly so that the Au and Cu potentials join smoothly along a line from Au center to Cu center. The value of the potential at the joining point was used for $\bar{V}$, the constant potential in the region between spheres.

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† This paper is a condensed version of a doctoral thesis submitted to Rensselaer Polytechnic Institute in August, 1966 by one of the authors (D.G.).

* This work was supported by the U. S. Atomic Energy Commission.

‡ Now at Watervliet Arsenal, Watervliet, New York.

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